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ATMOSPHERIC MEASUREMENTS OF SELECTED HAZARDOUS ORGANIC CHEMICALS

Interim Report - 1980

by

H. B. Singh
L. J. Salas
A. Smith
R. Stiles
H. Shigeishi

Atmospheric Science Center
SRI International
Menlo Park, California 94025

Cooperative Agreement 805990

Project Officer

Larry Cupitt
Atmospheric Chemistry and Physics Division
Environmental Sciences Research Laboratory
U. S. Environmental Protection Agency
Research Triangle Park, North Carolina 27711

ENVIRONMENTAL SCIENCES RESEARCH LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U. S. ENVIRONMENTAL PROTECTION AGENCY
RESEARCH TRIANGLE PARK, NORTH CAROLINA 27711

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Methods were developed for the accurate analysis of an expanded list of hazardous organic chemicals in the ambient air. On-site analysis using an instrumented mobile laboratory was performed for a total of 44 organic chemicals. Twenty of these are suspected mutagens or carcinogens. Toxicity studies for several others are currently pending. Six important meteorological parameters were also measured. Four field studies, each about two-weeks duration, were conducted in Houston, Texas; St. Louis, Missouri; Denver, Colorado; and Riverside, California. An around-the-clock measurement schedule (24 hours per day, seven days a week) was followed at all sites, permitting extensive data collection. Widely varying weather conditions facilitated observations of pollutant accumulation and wide variabilities in concentrations of pollutants at a given site. Concentrations, variabilities, and human exposure (daily dosages) were determined for all measured pollutants. The diurnal behavior of pollutants was studied. Average daily outdoor exposure levels of all four sites were determined to be 197 µg/day for halomethanes (excluding chlorofluorocarbons), 140 µg/day for haloethanes and halopropanes, 89 µg/day for chloroalkenes, 32 µg/day for chloroaromatics, 1,394 µg/day for aromatic hydrocarbons, and 479 µg/day for secondary organics. Exposure levels at Houston, Denver, and Riverside were comparable, but levels were significantly lower at St. Louis.

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ABSTRACT

During the second year of this project, methods were developed for the accurate ambient analysis of an expanded list of hazardous organic chemicals. On-site analysis using an instrumented mobile laboratory was performed for a total of 44 organic chemicals. Twenty of these are suspected mutagens or carcinogens. Toxicity studies for several others are currently pending. Six important meteorological parameters were also measured. Four field studies, each of about two-weeks duration, were conducted in Houston, Texas; St. Louis, Missouri; Denver, Colorado; and Riverside, California. A round-the-clock measurement schedule (24 hours per day, seven days a week) was followed at all sites, permitting extensive data collection. Widely varying weather conditions facilitated observations of pollutant accumulation and wide variabilities in concentrations of pollutants at a given site. Concentrations, variabilities, and human exposure (daily dosages) were determined for all measured pollutants. The diurnal behavior of pollutants was studied. Average daily outdoor exposure levels of all four sites were determined to be 197 μg/day for halomethanes (excluding chlorofluorocarbons, 140 μg/day for haloethanes and halopropanes, 89 μg/day for chloroalkenes, 32 μg/day for chloroaromatics, 1,394 μg/day for aromatic hydrocarbons, and 479 μg/day for secondary organics. Exposure levels at Houston, Denver, and Riverside were comparable, but levels were significantly lower at St. Louis.

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SECTION 1

INTRODUCTION

A vast number of potentially harmful organic chemicals are released into the environment, and it is becoming increasingly apparent that these chemicals contribute to the growing rate of cancer in industrialized countries. Despite recent and intense interest in toxic chemicals, the atmospheric abundance and fate of this important group of pollutants remains poorly understood. The purpose of this study project is to characterize the concentrations of a wide range of toxic organic chemicals at several urban and source-specific locations under varying meteorological and source-strength conditions. The measurement of these toxic chemicals is being conducted by in-situ analysis of ambient air using a suitably outfitted mobile laboratory. The overall program of analytical methods development, field measurements, data collection, and analysis is expected to provide information that will permit determination of the atmospheric abundance and chemistry of this potentially harmful group of chemicals.

The research plan is primarily designed to answer the following basic questions:

- What are the concentration levels and variabilities of selected toxic organic chemicals in typical urban environments?
- What are the atmospheric fates of these chemicals?
- What is the extent of human exposure to selected toxic chemicals?

The answers to these questions will be sought through a combination of approaches:

- A comprehensive program of field measurements at several urban locations and near several source-specific locations.
- Analysis of data collected during the field measurements and integration of this information with data acquired from outside sources.
- Compilation of all available information dealing with the sources, sinks, chemistry, and effects (health as well as environmental) of the toxic chemicals of interest.

This summary report presents the results accomplished during the second year of a three-year research effort. Analysis of data collected during the second year is by no means complete: Additional analysis will be presented in forthcoming reports and publications.

SECTION 2

OVERALL OBJECTIVES

The overall objectives of the proposed study are to:

- Characterize the abundance and variabilities of selected toxic organic chemicals in urban environments.
- Investigate and assess the atmospheric fates (sources and sinks) of these toxic chemicals.
- Determine the extent of human exposure.

To achieve these objectives, SRI will use the following approach:

- Develop and standardize new and improved procedures for sampling and analyzing toxic chemicals.
- Measure the atmospheric concentrations of toxic chemicals at several representative locations to develop a valid data base for ambient levels of toxic chemicals, and use these measurements to better understand the atmospheric fates of these chemicals.
- Update, validate, and assimilate information of production, emissions, atmospheric abundance, fates, and effects of toxic chemicals based on a continued program of literature search and information gathering.
- Develop and synthesize information on sources, removal mechanisms, extent of exposure, and health effects suggested by the preceding tasks.

SECTION 3

SECOND YEAR RESEARCH SUMMARY

The second-year research effort comprised a program of analytical methods development, field-data collection, data processing, and data interpretation for an expanded set of hazardous organic chemicals. All field measurements were conducted in-situ with the help of an instrumented mobile laboratory. After completion of the program of methods development, four field studies of roughly two-week duration each were conducted in Houston, Texas (Site 4); St. Louis, Missouri (Site 5); Denver, Colorado (Site 6); and Riverside, California (Site 7). These field studies were completed between early May and late July of 1980. The studies were designed to complement the three field studies conducted during the first year of this project at Los Angeles, California (Site 1); Phoenix, Arizona (Site 2); and Oakland, California (Site 3). Continuing practice of the first-year research, all field work in the second year was performed on a round-the-clock basis (24 hours per day, seven days a week), permitting the efficient collection of a large amount of data. A total of 44 organic chemicals and 5 meteorological parameters were measured. Over 20 of these chemicals are either mutagens or suspected carcinogens; in many other cases toxicity studies are currently incomplete.

Table 1 summarizes the average concentrations measured at each of the sites and the daily average outdoor exposure based on a total air intake of 23 m^3/day for a 70 kg male. The corresponding standard deviations associated with these parameters are shown in Table 1. The mutagenicity and toxicity information for individual species is also summarized in Table 1. It is pertinent to note that roughly 90 percent of mutagens are found to be carcinogens (McCann and Ames, 1977). Table 2 summarizes average exposure (μg/day) to individual categories of chemical groups at each of the sites. Overall, the total exposure to measured toxic chemicals at Houston, Denver, and Riverside was comparable (it was significantly lower at St. Louis). As a category, exposure to aromatic hydrocarbons is the highest, and to chloroaromatics the lowest, at all sites.

Hot-spots for specific toxic chemicals are found at different locations. As is clear from Table 1, the ambient levels of 1,2-dichloroethane (a suspected carcinogen) were significantly elevated at the Houston site despite meteorological conditions that were unfavorable to pollutant accumulation. Hot-spots of methylene chloride (a weak mutagen) and chloroform (a suspected carcinogen) were observed at Riverside. The high concentrations of chloroform at Riverside are surprising. (No large sources are known.) Special tests were conducted to ensure the reliability of these data: Chloroform data were found to be accurate to within ±10 percent. Formaldehyde, another suspected carcinogen, was measured at high concentrations at all sites.

TABLE 1. CONCENTRATIONS, DAILY EXPOSURES, AND TOXIC EFFECTS OF MEASURED HAZARDOUS ORGANIC CHEMICALS

Chemical Group and Species	Houston – Site 4 (14–25 May 1980)				St. Louis – Site 5 (29 May–9 Jun 1980)				Denver – Site 6 (10–20 Jun 1980)				Riverside – Site 7 (1–13 July 1980)				Toxicity
	Concentration (ppt)		Daily Exposure* (µg/day)		Concentration (ppt)		Daily Exposure (µg/day)		Concentration (ppt)		Daily Exposure (µg/day)		Concentration (ppt)		Daily Exposure (µg/day)		
	Average	S.D.‡	Average	S.D.	Average	S.D.	Average	S.D.	Average	S.D.	Average	S.D.	Average	S.D.	Average	S.D.	
Chlorofluorocarbons																	
Trichlorofluoromethane (F11)	474	178	98.6	11.5	374	166	46.6	7.1	637	256	82.2	16.2	671	318	87.6	19.9	These chlorofluorocarbons are not considered to be toxic but possess excellent properties as tracers of urban air masses
Dichlorofluoromethane (F12)	887	474	103.5	30.2	622	182	68.7	12.5	1005	565	107.0	24.5	1050	401	126.2	35.0	
Trichlorotrifluoroethane (F113)	199	160	37.7	26.5	132	171	21.9	5.1	221	235	46.0	21.3	274	262	44.6	11.5	
Dichlorotetrafluoroethane (F114)	26	10	4.5	0.9	25	6	4.0	0.5	34	9	5.5	0.8	29	9	4.8	1.0	
Halomethanes																	
Methyl chloride	986	403	46.5	16.3	732	138	34.1	1.2	783	132	36.8	4.8	705	170	34.8	8.3	BM
Methyl bromide	100	50	9.3	3.3	61	25	7.2	1.2	124	51	11.2	3.4	200	167	23.5	12.3	BM
Methyl iodide	2.6	2.2	0.4	0.2	2.6	1.6	0.4	0.2	1.8	1.0	0.2	0.0	2.8	1.2	0.4	0.2	SC, BM
Methylene chloride	574	553	43.0	24.6	421	583	29.3	10.5	967	936	76.1	34.6	1949	1488	158.1	53.7	BM
Chloroform	423	749	42.8	34.6	73	39	7.9	1.8	185	266	18.0	9.2	703	798	76.1	44.3	SC, BM
Carbon tetrachloride	494	449	61.6	43.4	129	6	18.5	0.9	174	19	25.2	1.4	175	23	25.2	1.6	SC, NBM
Haloethanes and halopropanes																	
Ethyl chloride	227	273	13.5	8.0	46	29	2.7	1.1	41	24	2.4	0.8	87	66	5.1	1.9	–
1,1 Dichloroethane	63	20	6.1	1.1	60	14	5.6	0.9	65	31	6.3	1.6	66	22	6.1	1.1	NBM
1,2 Dichloroethane	1512	1883	125.0	81.1	124	101	11.4	4.7	241	297	20.3	8.6	357	325	31.8	12.3	SC, BM
1,2 Dibromoethane	58	72	9.9	5.6	16	4	2.8	0.4	31	15	5.5	0.9	22	7	3.9	0.5	SC
1,1,1 Trichloroethane	383	263	41.5	12.8	235	136	26.0	7.1	713	563	92.3	31.2	747	257	82.8	17.8	Weak BM
1,1,2 Trichloroethane	32	24	3.1	1.8	15	6	1.9	0.4	27	10	3.4	0.8	41	21	5.0	2.1	SC, NBM
1,1,1,2 Tetrachloroethane	12	15	1.1	0.8	6	3	0.3	0.3	10	12	0.9	0.9	9	3	1.1	0.3	NBM
1,1,2,2, Tetrachloroethane	11	9	1.6	0.7	6	2	0.3	0.2	10	3	0.8	0.3	12	9	1.4	0.3	SC, BM
1,2 Dichloropropane	81	37	8.5	1.4	53	12	5.6	0.7	48	19	5.2	1.2	57	15	6.0	1.0	BM
Chloroalkenes																	
Vinylidene chloride	25	30	1.4	1.1	9	5	0.4	0.2	31	49	?	4.0	9	6	0.5	0.3	SC, BM
(cis) 1,2 Dichloroethylene	71	59	6.3	2.6	30	8	3.5	0.5	76	61	7.3	2.4	60	14	5.4	0.6	NBM
Trichloroethylene	144	196	16.2	10.6	112	184	13.5	7.4	198	313	23.4	31.2	118	55	14.5	3.2	SC, BM
Tetrachloroethylene	401	588	61.4	61.9	326	955	58.4	72.0	394	168	58.5	11.4	484	236	76.7	20.8	SC
Allyl chloride	<5	–	<0.4	–	<5	–	<0.4	–	<5	–	<0.4	–	<5	–	<0.4	–	SC
Hexachloro-1,3 butadiene	11	20	2.7	2.7	3	2	0.7	0.2	2	1	0.5	0.2	4	3	1.1	0.3	BM
Chloroaromatics																	
Monochlorobenzene	308	517	34.4	24.8	240	343	23.0	10.3	290	217	27.6	12.4	–	–	–	–	–
o-Chlorotoluene	<5	<5	<0.6	–	<5	–	<0.6		<5	–	<0.6		<5	–	<0.6		BM
o-Dichlorobenzene	7	9	1.0	0.7	6	11	0.8	0.6	26	34	4.3	2.9	10	8	1.4	0.4	–
m-Dichlorobenzene	7	8	0.7	0.3	4	8	0.3	0.3	8	7	1.0	0.6	6	4	0.6	0.3	–
p-Dichlorobenzene	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
1,2,4 Trichlorobenzene	2	2	0.4	0.1	1	1	0.2	0.0	6	4	1.0	0.5	10	7	1.7	0.3	–
Aromatic hydrocarbons																	
Benzene	5780	5880	449.2	283.3	1410	1190	91.0	48.4	4300	3940	302.4	139.9	3960	1910	280.4	63.9	SC
Toluene	10330	10850	822.4	419.9	1520	1250	126.0	64.9	6240	5280	511.6	173.1	5800	3670	498.9	155.6	–
Ethyl benzene	1380	1400	130.7	94.8	640	460	44.9	23.9	2220	3130	195.5	94.8	1330	820	127.7	30.9	–
m/p Xylene	3940	4270	362.1	219.4	980	703	86.8	50.9	2860	3320	263.3	139.6	2231	1515	215.5	52.9	–
o Xylene	1307	1460	123.7	65.8	310	300	21.9	11.0	1290	1210	112.7	50.9	1100	650	102.7	22.9	–
4-Ethyl toluene	870	1030	80.3	44.0	240	180	19.2	11.3	930	780	88.1	31.6	820	460	86.8	22.6	–
1,2,4 Trimethyl benzene	1190	1470	116.6	54.2	370	370	12.4	26.0	1410	2310	122.0	74.5	740	500	78.4	50.7	–
1,3,5 Trimethyl benzene	490	900	27.1	21.5	530	490	20.2	13.6	340	240	20.3	11.3	230	170	13.6	5.6	–
Oxygenated species																	
Formaldehyde	–	–	–	–	11300	4900	319.0	127.0	12300	5900	347.0	167.0	19000	7600	536.0	215.0	SC, BM
Phosgene	<20	–	<1	–	<20	–	<1	–	<20	–	<1	–	≈50	–	2.5	–	–
Peroxyacetylnitrate (PAN)	438	835	44.0	46.4	277	203	24.4	8.0	443	1246	45.0	21.4	1196	1249	138.8	40.8	Phytotoxic
Peroxypropionylnitrate (PPN)	110	140	6.5	6.0	84	93	0.5	1.2	45	47	4.4	2.7	183	197	19.2	8.3	Phytotoxic

*Daily average exposure based on total air intake of 23 m^3/day at 25°C and 1 atm pressure

†BM Bacterial Mutagen, Positive mutagenic activity based on Ames salmonella mutagenicity test
NBM (Not Bacterial Mutagen) Negative response in the Ames salmonella mutagenicity test
SC Suspected Carcinogens

‡Standard deviation

TABLE 2. SUMMARY OF EXPOSURE TO HAZARDOUS ORGANIC CHEMICAL GROUPS

Chemical Category*	Total Average Daily Exposure (μg/day)				
	Houston – Site 4	St. Louis – Site 5	Denver – Site 6	Riverside – Site 7	Average of Sites
Chlorofluorocarbons†	205	141	241	262	212
Halomethanes	203	97	168	319	197
Haloethanes and halopropanes	210	59	137	153	140
Chloroalkenes	88	78	92	98	89
Chloroaromatics	37	25	34	–	32
Aromatic hydrocarbons	2130	430	1616	1401	1394
Oxygenated species	–	344	396	696	479

*As defined in Table 1

†NOT suspected to be directly toxic

To the extent that urban data can act as an early warning indicator of emissions, it appears that the use of fluorocarbon 113 has significantly increased. Typical fluorocarbon 12 and fluorocarbon 113 ratios are 1/2 to 1/3 of what should be expected, based on known emission information.

In order to assess the atmospheric fates of measured toxic chemicals, mean diurnal variations of these substances were studied at each of the sites. These results are discussed in the text. It is clear, however, that the atmospheric abundance of hazardous organic chemicals at a given site can vary by an order of magnitude or more depending upon the source strength, chemical lifetime, and the prevailing weather conditions. The spectrum of chemicals measured is very similar in all urban atmospheres, although exposures can vary significantly.

SECTION 4

ANALYTICAL METHODOLOGY

TRACE CONSTITUENTS OF INTEREST

The target chemicals that were measured during the second year of research were those suspected of being hazardous or chemicals structurally similar to these. In many cases, toxicity data are currently unavailable or pending. Our ability to satisfactorily measure a trace constituent at its expected ambient concentration was also an essential requirement for its inclusion in this work. No data are reported on $p\text{-}C_6H_4Cl_2$ because atmospheric interferences prevented rigorous quantification. Preliminary efforts were also made to measure acrylonitrile in the ambient environment; however, this attempt was abandoned after we concluded that existing measurement methods are unsuited for ambient analysis.

A total of 44 trace chemicals were targeted and are categorized in Table 3. The categories include chlorofluorocarbons, halomethanes, haloethanes, halopropanes, chloroalkenes, chloroaromatics, aromatic hydrocarbons, and oxygenated and nitrogenated species. The chlorofluorocarbons are considered to be nontoxic but are excellent tracers of polluted air masses. Formaldehyde was the only aldehyde measured, although work is in progress to develop measurement methods utilizing liquid chromatographic techniques for other aliphatic and aromatic aldehydes. A number of important meteorological parameters (wind speed, wind direction, temperature, pressure, relative humidity, and solar flux) were also measured.

It is obvious from Table 3 that a large number of targeted chemicals are either mutagens or suspected carcinogens (Helmes et al., 1980). It is pertinent to add here that 90 percent of the mutagens are found to be carcinogens and 90 percent of noncarcinogens are found to be nonmutagens (McCann and Ames, 1977). Assuming a nonthreshold carcinogenic response, unit risk factors for several carcinogens can be determined. A unit lifetime risk factor (f) is obtained by extrapolating animal bioassay data to humans. The risk factors computed for a healthy male (70-kg weight) when exposed to 1 $\mu g/m^3$ of a carcinogen are listed in Table 4 (Padgett, 1979) for a select group of carcinogens targeted for study here. The yearly deaths in a given population that is exposed to a carcinogen can be computed from the equation

$$\text{computed deaths} = fpe/l \quad ,$$

where p = population at risk, e = average exposure ($\mu g/m^3$); l = average lifetime ($\simeq$ 70 years). Currently, risk factors are highly uncertain, and

TABLE 3. TARGET CHEMICALS FOR SECOND-YEAR RESEARCH

Chemical Name*	Chemical Formula	Toxicity†
Chloro-Fluorocarbons		
Trichloromonoflouromethane (F11)	CCl_3F	These chlorofluorocarbons are nontoxic but have excellent properties as tracers of urban air masses
Dichlorodiflouromethane (F12)	CCl_2F_2	
Trichlorotrifluoroethane (F113)	CCl_2FCClF_2	
Dichlorotetrafluoroethane (F114)	$CClF_2CClF_2$	
Halomethanes		
Methyl chloride	CH_3Cl	BM*
Methyl bromide	CH_3Br	BM
Methyl iodide	CH_3I	SC†, BM
Methylene chloride	CH_2Cl_2	BM
Chloroform	$CHCl_3$	SC, BM
Carbon tetrachloride	CCl_4	SC, NBM†
Haloethanes and halopropanes		
Ethyl chloride	C_2H_5Cl	–
1,1 Dichloroethane	$CHCl_2CH_3$	NBM
1,2 Dichloroethane	CH_2ClCH_2Cl	SC, BM
1,2 Dibromoethane	CH_2BrCH_2Br	SC
1,1,1 Trichloroethane	CH_3CCl_3	Weak BM
1,1,2 Trichloroethane	$CH_2ClCHCl_2$	SC, NBM
1,1,1,2 Tetrachloroethane	$CHClCCl_3$	NBM
1,1,2,2 Tetrachloroethane	$CHCl_2CHCl_2$	SC, BM
1,2 Dichloropropane	$CH_2ClCHClCH_3$	BM
Chloroalkanes		
Vinyledene chloride	$CH_2=CCl_2$	SC, BM
(cis) 1,2 Dichloroethylene	$CHCl=CHCl$	NBM
Trichloroethylene	$CHCl=CCl_2$	SC, BM
Tetrachloroethylene	$CCl_2=CCl_2$	SC
Allyl chloride	$ClCH_2CH=CH_2$	SC
Hexachloro-1,3 butadiene	$Cl_2C=CCl-CCl=CCl_2$	BM
Chloroaromatics		
Monochlorobenzene	C_6H_5Cl	–
α-Chlorotoluene	$C_6H_5CH_2Cl$	BM
o-Dichlorobenzene	$o\text{-}C_6H_4Cl_2$	–
m-Dichlorobenzene	$m\text{-}C_6H_4Cl_2$	–
p-Dichlorobenzene	$p\text{-}C_6H_4Cl_2$	–
1,2,4 Trichlorobenzene	$1,2,4\ C_6H_3Cl_3$	–
Aromatic hydrocarbons		
Benzene	C_6H_6	SC
Toluene	$C_6H_5CH_3$	–
Ethyl benzene	$C_6H_5C_2H_5$	–
m/p-Xylene	$m/p\text{-}C_6H_4(CH_3)_2$	–
o-Xylene	$o\text{-}C_6H_4(CH_3)_2$	–
4-Ethyl toluene	$4\text{-}C_6H_4C_2H_5CH_3$	–
1,2,4 Trimethyl benzene	$1,2,4\ C_6H_3(CH_3)_3$	–
1,3,5 Trimethyl benzene	$1,3,5\ C_6H_3(CH_3)_3$	–
Oxygenated and nitrogenated species		
Formaldehyde	$HCHO$	SC, BM
Phosgene	$COCl_2$	–
Peroxyacetyl nitrate (PAN)	$CH_3COOONO_2$	Phytotoxic
Peroxypropionyl nitrate (PPN)	$CH_3CH_2COOONO_2$	Phytotoxic
Acrylonitrile‡	$CH\equiv CN$	SC

*In addition to chemical species, meteorological parameters were measured. These were: wind speed, wind direction, temperature, pressure, relative humidity and solar flux

†BM: Positive mutagenic activity based on Ames salmonella mutagenicity test (Bacterial Mutagens)
NBM: Not found to be mutagens in the Ames salmonella test (Not Bacterial Mutagens)
SC: Suspected Carcinogens

‡Satisfactory measurement method for ambient analysis is not available

TABLE 4. ESTIMATED UNIT RISK FACTORS FOR SELECTED CARCINOGENS

Chemical	Unit Risk Factor, f*
Chloroform	4.6×10^{-6}
Carbon tetrachloride	1.2×10^{-6}
1,2 Dichloroethane	1.2×10^{-5}
1,2 Dibromoethane	5.9×10^{-4}
Vinyl chloride	4.1×10^{-6}
Vinyledene chloride	2.5×10^{-5}
Trichloroethylene	4.2×10^{-6}
Tetrachloroethylene	7.6×10^{-6}
Allyl chloride	9.9×10^{-6}
Benzene	7.0×10^{-6}
Formaldehyde	3.4×10^{-5}

Source: Padgett (1979)

*Computed for a healthy male (70-kg weight) when exposed to an average 1-$\mu g/m^3$ exposure over an extended period

insufficient exposure information is available to compute deaths caused by carcinogens. However, those given here are useful for relative comparison.

FIELD INSTRUMENTATION

One of the primary motivations of our study was to conduct in-situ analysis of trace chemicals, to minimize the many problems that arise when samples are collected in vessels or in tubes filled with solid sorbents and analyzed after long delays. It is widely agreed that the integrity of the air samples is assured when careful in-situ analysis is performed.

All field work was therefore conducted in an in-situ mode using a suitably instrumented mobile environmental laboratory. Table 5 summarizes the equipment that was available on our mobile laboratory for the conduct of this study. This laboratory was air conditioned for temperature control and operated on a 220-V, 80-A circuit. Provision was also devised for operating on 110-V input. A 200-m electrical cord was always used to station the laboratory away from the electrical source or a power pole. The sampling manifold was all stainless steel with a variable inlet height. In all cases the sampling manifold was adjusted to be higher than nearby structures: A typical manifold inlet height was 5 m above ground. For pumping and pressuring air samples, a special stainless-steel metal bellows compression pump (Model MB 158) was always used.

TABLE 5. ENVIRONMENTAL MOBILE LABORATORY INSTRUMENTATION*

Instrument	Features	Analysis
Perkin Elmer 3920 GC1	2 ECD†, 1 dual FID‡	Trace constituents
Perkin Elmer 3920 GC2	2 ECD, 1 dual FID	Trace constituents
Perkin Elmer 3920 GC3 (capillary column GC)	2 ECD, 1 dual FID	Trace constituents
Coulometric dual EC-GC	Coulometric ECD	Halocarbons, PAN, PPN, $COCl_2$; calibration
Beckman 6800	FID	CO-CH_4-THC
Horiba AIA-24	NDIR§	CO, CO_2
Bendix 8101-B	Chemiluminescent	NO, NO_2
Monitor Labs Model 8440E	Chemiluminescent	NO and NO_2
Dasibi Model 1003 AH	Photometric principle	Ozone
AID Model 560	Chemiluminescent	Ozone
Bendix 8002	Chemiluminescent	O_3
Eppley pyranometer		Solar flux
Eppley UV radiometer		Ultraviolet radiative flux
Miscellaneous meteorological equipment		Wind speed, wind direction, temp, pressure, dew point, relative humidity
Auto Lab IV Data System (No. 1)		GC data
SP-4000 Multichannel Data System (No. 2)		GC data
Digitem Data System (No. 3)		All continuous air quality and meteorological data
Stainless-steel manifold		Sampling of HCs and halocarbons
Teflon manifold		Sampling O_3, NO, NO_x

*Note: Finnigan 3200 GC/MS available to this project at SRI

†Electron capture detector

‡Flame ionization detector

§Nondispersive infrared

EXPERIMENTAL PROCEDURES

Air Analysis

For all halogenated species and organic nitrogen compounds shown in Table 3, electron-capture detector (ECD) gas chromatography (GC) was the primary means of analysis. The aromatic hydrocarbons were measured using flame-ionization detector (FID) gas chromatography. Formaldehyde was the only species measured by the wet chemical analysis technique utilizing the chromotropic acid procedure (U.S. Public Health Science, 1965). Under normal operating conditions 5 GC channels were operated with ECDs and only one with FID. Although the exquisite sensitivity of the ECD would allow the determination of several species in Table 3 with a direct 5-ml injection of air, preconcentration of air samples was necessary for efficient operation. All six GC channels were equipped with stainless-steel sampling valves and could be operated either with a direct sampling loop or with a preconcentration trap. In no instance was a sample size of greater than 1 liter used: In most cases, sample volumes of 500 ml or less were satisfactory. Sample preconcentration was conducted on a 4-inch-long bed of 100/120 mesh glass beads packed in a 1/16-inch diameter stainless-steel tubing maintained at liquid oxygen temperature. The glass beads could be replaced with an equivalent length of SE-30 packing (3 percent SE-30 on 100/120 mesh acid-washed chromosorb W) or glass wool with completely satisfactory results. Desorption of chemicals from the preconcentration traps was accomplished by holding the trap at boiling-water temperature and purging with carrier gas.

The sampling was achieved by pressurizing a 1-liter stainless-steel canister to 32 psi. The sampling line and the pretrap (maintained at 90°C) were flushed with ambient air and the canister pressure brought to 30 psi. Sampling then began. The preconcentration trap was immersed in liquid oxygen and an air volume sampled from pressure p_1 to p_2. A high-precision pressure gauge (±0.05 psi) was used to measure the canister pressure. A typical setting was $p_1 = 30.0$ psi and $p_2 = 24.0$ psi. Ideal gas laws were found to hold excellently at these pressures and were used to estimate sample volumes. The pressure range of 30 to 20 psi assured smooth flow through the preconcentration traps without problems of plugging. All other sampling was accomplished by using sampling loops that were flushed with all-glass syringes of 100-ml volume.

Table 6 summarizes methods used for the analysis of trace species. The GC condition used are also stated. Because of the dominant water response of the ECD, a post-column Ascarite trap was inserted to remove water from halocarbon analysis. No water trap was used for the analysis of aromatic hydrocarbons, PAN, PPN, and phosgene.

The identity of trace constituents was established by using the following criteria:

- Retention times on multiple GC columns (minimum of two columns)
- EC thermal response

TABLE 6. ANALYTICAL CONDITIONS FOR THE ANALYSIS OF SELECTED TOXIC CHEMICALS

GC Column				Detector		Typical Carrier Gas Flow Rate (ml/min)	Typical Sample Size (ml)	Remarks
No.	Description	Temp. (°C)	Species Measured	Type	Temp. (°C)			
1	6 ft X 1/8 in, SS,* 20% SP2100, 0.1% CW 1500 on 100/120 mesh Supelcoport	45	$CHCl_3$; CH_3CCl_3; CCl_4; cis-CHClCHCl, C_2HCl_3; $CH_2ClCHCl_2$; C_2Cl_4; CH_3CHCl_2; CH_2ClCCl_3; $CHCl_2CHCl_2$; $CH_2ClCHClCH_3$	Electron capture	275	40	500	No water trap
2	33 ft X 1/8 in, Ni, 20% DC 200 on 80/100 mesh Supelcoport	45	CH_3Cl; CH_3Br; CH_2CCl_2; CH_3I; CCl_3F; CCl_2F_2; $CClF_2CCl_2F$; $CClF_2CClF_2$	Electron capture	275	25	500	Ascarite water trap
3	6 ft X 1/8 in, SS, 10% N, N, -bis (2-cyanoethyl) Formamide on Chromosorb P (A/W)	65	C_6H_6; $C_6H_5CH_3$; m/p/o-$C_6H_4(CH_3)_2$; 4-$C_6H_4C_2H_5$; 1,3,5 $C_6H_3(CH_3)_3$; 1,2,4 $C_6H_3(CH_3)_3$	Flame ionization	275	45	500	No water trap
4	3 ft X 1/8 in, Ni, 5% SP 1200 -5% Bentone on 100/120 mesh Supelcoport	65	C_6H_5Cl; m-$C_6H_4Cl_2$; o-$C_6H_4Cl_2$; 1,2,4 $C_6H_3Cl_3$; $C_6H_5CH_2Cl$; $CCl_2CClCClCCl_2$	Electron capture	275	45	750	No water trap
5	15 ft X 1/8 in, SS, 10% SP 1000 on 100/120 mesh Supelcoport	45	CH_2ClCH_2Cl	Electron capture	265	25	100	Ascarite water trap
6	10 ft X 1/8 in, SS, 0.2% CW 1500 80/100 mesh on carbopack C	45	CH_2Cl_2; CCl_3F; cis-CHClCHCl; CH_3I; CCl_2FCClF_2; CH_3CCl_3; CCl_4; C_2H_5Cl; CH_2CHCH_2Cl	Electron capture	265	40	10	Ascarite water trap; also used for CH_2CCl_2 measurement with preconcentration
7	10 in X 1/4 in, Teflon, 5% CW 400, on 60/80 mesh Chromosorb W(A/W)	30	PAN, PPN	Electron capture	30	60	5	No water trap
8	5 ft X 1/4 in, SS, 30% didecyl phthalate, 100/120 mesh, Chromosorb P (A/W)	30	$COCl_2$	Electron capture	30	70	5	No water trap

*Stainless steel

- EC ionization efficiency
- Limited GC/MS analysis.

Details of these comparisons for halocarbon species, organic nitrogen compounds, and aromatic hydrocarbons have already been published and need not be repeated here (Singh et al., 1979).

CALIBRATIONS

Calibrations for all species were performed using three basic methods:

- Permeation tubes
- Multiple dilutions
- Gas-phase coulometry.

As reported earlier (Singh et al., 1979), permeation tubes provide the best means to generate low-ppb primary standards for a significant number of chemicals listed in Table 3. However, these were unacceptable for a large number of species. Based on our previous experience, we concluded that unacceptable permeation tubes could operate satisfactorily at high temperatures. Therefore, two temperature baths maintained at 30.0 ±0.05°C and 70.0 ±0.1°C were installed. The 30°C bath was a water bath, and the 70°C bath was an oil bath. All permeation tubes were contained in specialized holders and were purged continuously with a prepurified gas (He, air, or N_2) flowing at 50 to 80 ml/min. A large-volume mixing chamber was installed at the permeation tube exit to allow for complete mixing. Syringe samples were withdrawn from the mixing chamber using all-glass syringes. With the installation of the 70°C bath, all permeation tubes performed excellently. Table 7 reports the measured permeation-rate data for each of the chemical constituents of interest. It is clear from Table 7 that many species (e.g. CCl_4, CH_3CCl_3, CH_2BrCH_2Br, chloroaromatics) for which permeation tubes could not be used earlier are now giving excellent results. Figure 1 demonstrates the excellent linearity of the permeation rate for some of these chemicals. Overall, we believe that this offers the best, most-accurate means of generating primary standards.

It is also clear from Table 7 that most of these permeation tubes can be used to prepare standards directly at parts per billion (ppb) concentration levels. Batch dilutions were carried out to reduce these concentrations by a factor of 10^2 to 10^3. Over a wide range of concentration levels of several ppb's and low ppt's, the frequency-modulated ECDs that we used were completely linear. The linearity of the FID over a much larger concentration range is well known.

In addition to permeation tubes, standards were obtained from Scott-Marrin (Riverside, California). These were obtained at higher concentrations (5 to 10 ppm) for reasons of long-term stability. Table 8 lists the chemicals, the standard concentrations, and the cylinder materials. All of the chemicals were stored in aluminum cylinders except those containing CH_3Cl, which were contained in stainless-steel cylinders. Extreme care was required

TABLE 7. PERMEATION RATE DATA FOR GENERATING PRIMARY STANDARDS

Compound	Permeation Tube Number or I.D.	Temperature, (°C*)	Permeation Rate		Status†	Quality†
			ng/min	ppb/l/min (25°C, 1 atm)		
CH_2=CHCHO	2356	30.0	969	423	S	E
CH_2OCH_2	1908	30.0	1120	618	S	E
CCl_2F_2 (F12)	6138	30.0	615	123	S	E
CCl_3F (F11)	1911	30.0	1680	299	S	E
$CHCl_2F$ (F21)	2347	30.0	942	224	S	E
$CHClF_2$ (F22)	2348	30.0	80	23	?	E
CCl_2FCClF_2 (F113)	1238	30.0	715	93	S	E
$CClF_2CClF_2$ (F114)	2345	30.0	6254	894	S	E
CH_3Cl	2355	30.0	1915	927	S	E
C_2H_5Cl	2350	30.0	480	182	S	E
CH_2CHCl	2352	30.0	1270	497	S	E
$ClCH_2CH$=CH_2	7497	30.0	142	45	S	E
CH_3Br	1893	30.0	2477	638	S	G
CH_3I	1239	30.0	109	19	S	G
CH_2Cl_2	2354	30.0	523	150	S	E
(cis) CHClCHCl	1939	30.0	2564	648	S	G
(trans) CHClCHCl	1898	30.0	1696	428	S	G
CCl_2CH_2	1897	30.0	731	184	S	G
CH_2ClCH_2Cl	1907	70.0	2622	648	S	E
CH_2ClCH_2Cl	1899	30.0	125	31	S	G
$CHCl_2CH_3$	2353	30.0	71	18	S	G
$CH_2ClCHClCH_3$	MET1	70.0	2456	531	S	E
(trans) CHCl=$CHCH_2Cl$	MET2	70.0	7906	1720	S	E
CCl_2	2351	30.0	942	233	S	E
$CHCl_3$	1229	30.0	174	36	S	G
C_2HCl_3	1235	30.0	314	58	S	E
CCl_3CH_3	1896	70.0	980	179	S	E
CCl_3CH_3	1589	70.0	3450	632	S	E
$CHCl_2CH_2Cl$	1901	30.0	129	24	S	G
CCl_4	1894	70.0	1983	315	S	E
C_2Cl_4	1902	70.0	3381	494	S	E
C_2Cl_4	1590	30.0	706	104	S	E
CH_2BrCH_2Br	1237	70.0	1220	180	S	E
$CHBr_3$	1895	70.0	1318	127	S	E
C_6H_5Cl	MET3	70.0	4607	980	S	E
$C_6H_5CH_2Cl$	MET4	70.0	1528	295	S	E
o-$C_6H_4Cl_2$	MET5	70.0	1369	226	S	E
m-$C_6H_4Cl_2$	MET6	70.0	2515	418	S	E
p-$C_6H_4Cl_2$	MET7	70.0	1586	265	S	E

NOTE: All permeation tubes were given a 2 week or longer conditioning time

*Temperature maintained to ± 0.05°C

†E–Excellent (errors in permeation rate < ±10%); G–Good (errors in permeation rate < ±15%); S-Satisfactory (±15 %)

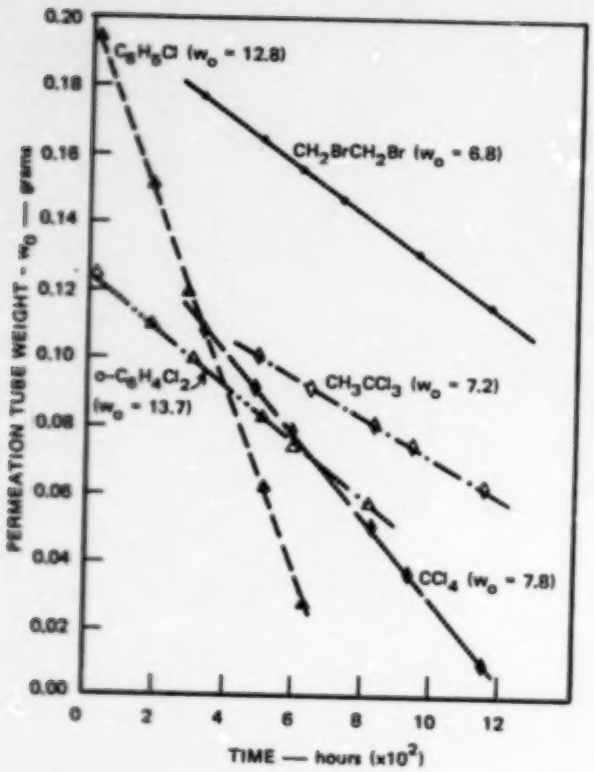

Figure 1. Permeation tube weight-time relationship for selected chemicals.

in selecting cylinder materials, since some of the chemicals (e.g., CH_3Cl) form unknown chemical complexes and could lead to potentially explosive conditions with aluminum.

All of the commercially obtained standards were rechecked with our permeation-tube standards when this was possible. The comparisons were found to yield excellent results (±10 percent). The aromatic hydrocarbon standards were checked for carbon response against those available from NBS and found to agree within ±5 percent. For other aromatic hydrocarbons carbon response derived from benzene and toluene responses was used.

For the chlorinated aromatics the Scott-Marrin standards were found to deteriorate over a period of several months. In the case of PAN and PPN, only gas-phase coulometry was used, and the data must be considered preliminary until the confirmation of the reliability of PAN and PPN determination using gas-phase coulometry can be established. In the meantime, these data do appear reasonable.

TABLE 8. PPM LEVEL PRIMARY STANDARDS IN AIR*

Standard and Compound†	Concentration (ppm)	Long-term Stability‡ (1-year period)	Cylinder	
			Type	Size (ft^3)
S1				
1,1,1 Trichloroethane	5.0	E	Aluminum	30
Carbon tetrachloride	5.2	P		
1,2 Dibromoethane	5.0	E		
Hexachloroethane	0.8	U		
S2				
Monochlorobenzene	5.0	P	Aluminum	150
o-dichlorobenzene	5.0	P		
S3				
Benzene	5.0	E	Aluminum	150
Toluene	5.0	E		
S4				
Methyl chloride	10.0	E	Stainless steel	30
Methylene chloride	10.0	E		
1,2 Dichloroethane	10.0	E		
S5				
Trichloroethylene	10.0	E	Aluminum	30
Tetrachloroethylene	10.0	E		
Chloroform	10.0	E		

*Obtained on order from Scott-Marrin, Inc., Riverside, California

†For all of these chemicals (except C_6H_6 and $C_6H_5CH_3$) satisfactory permeation tubes were also operational. Therefore, a majority of these standards were used more as secondary standards than as primary ones. For aromatic hydrocarbons, the Scott-Marrin standards were used as primary standards

‡E: excellent; P: poor; U: unknown

Secondary Standards

Except for the aromatic hydrocarbons, it was not possible to use primary standards during field operation. Therefore, an optimal scheme that depended on the use of secondary standards was devised.

A 35 liter and several 5-liter (as back-ups) polished stainless-steel samplers were filled with urban air samples to a pressure of 35 to 40 psi.

These were allowed to stabilize for one to two days and then analyzed by comparing them against the primary standards. The 35-liter pressurized secondary standard was then used for field operation: Each GC channel was calibrated about 3 times a day with this secondary standard. The stability of nearly all species over a period of several days was found to be excellent. Some species, such as PAN, PPN, or $COCl_2$, could not be stored for any reasonable length of time. This was not a serious hinderance since other chemicals could be used to ascertain the constancy of the ECD and the FID responses during field operations. All of the Scott-Marrin standards were also carried on board after these had been diluted to low ppb levels. These were also used as secondary standards (in addition to the collected air samples). The stability of the diluted Scott-Marrin cylinders (in polished 1- to 5-liter stainless steel vessels) was found to be excellent. Analysis of these prior to field experimentation, during field studies, and after the completion of field studies did not show a charge from the measurement precision under field conditions.

QUALITY CONTROL

Two major factors were critical in establishing the quality of the acquired date: the accuracy of primary standards and precision and repeatability of measurements. As stated earlier in this section, the primary standards commercially obtained were compared with our permeation tubes which can be routinely used to obtain reliable standards within errors of ±5 to 10 percent. The aromatic hydrocarbon standards were compared with NBS propane standards and found to be accurate to within ±5 percent. The cross-calibrations between SRI generated standards and Scott-Marrin standards typically results in differences of about ±10 percent or less. The use of secondary standards nearly three times a day clearly demonstrated the excellent precision that was obtainable during field studies. The precision of reported field measurements is estimated to be ±5 percent. The measurements presented here have an overall estimated accuracy of better than ±15 percent.

SECTION 5

PLAN OF FIELD MEASUREMENTS

The first quarter of this project was devoted to developing methods for accurately analyzing a comprehensive list of toxic chemicals and to procuring supplies and equipment for the four planned field studies.

After the measurement methodology was developed, field studies were conducted in selected urban sites. The four sites selected were in Houston, Texas; St. Louis, Missouri; Denver, Colorado; and Riverside, California. In all cases, the sites represented an open urban atmosphere. There were no nearby sources or topographical features that could directly affect the representativeness of the measurements. Figure 2 shows the location of these sites. Each field study was of about two-weeks duration. Despite the logistical difficulty, a 24-hour measurement schedule offers the most efficient means of collecting the maximum amount of data to characterize the burden of toxic organic chemicals in the ambient air. In addition, night abundances of trace chemicals are likely to provide crucial information about the sources and sinks of measured species. Therefore, during all field programs a 24-hour-per-day, seven-days-a-week measurement schedule was followed.

Although meteorological analysis has not yet been completed, general weather conditions were not unusually severe. In Houston, rainfall and passage of fronts did not allow for severe pollution episodes. St. Louis weather produced relatively clean environmental conditions. Weather in Denver was moderately hot and stagnant. At Riverside, the first half of the study period exhibited relatively clean conditions; the second half was more representative of hot and somewhat stagnant conditions.

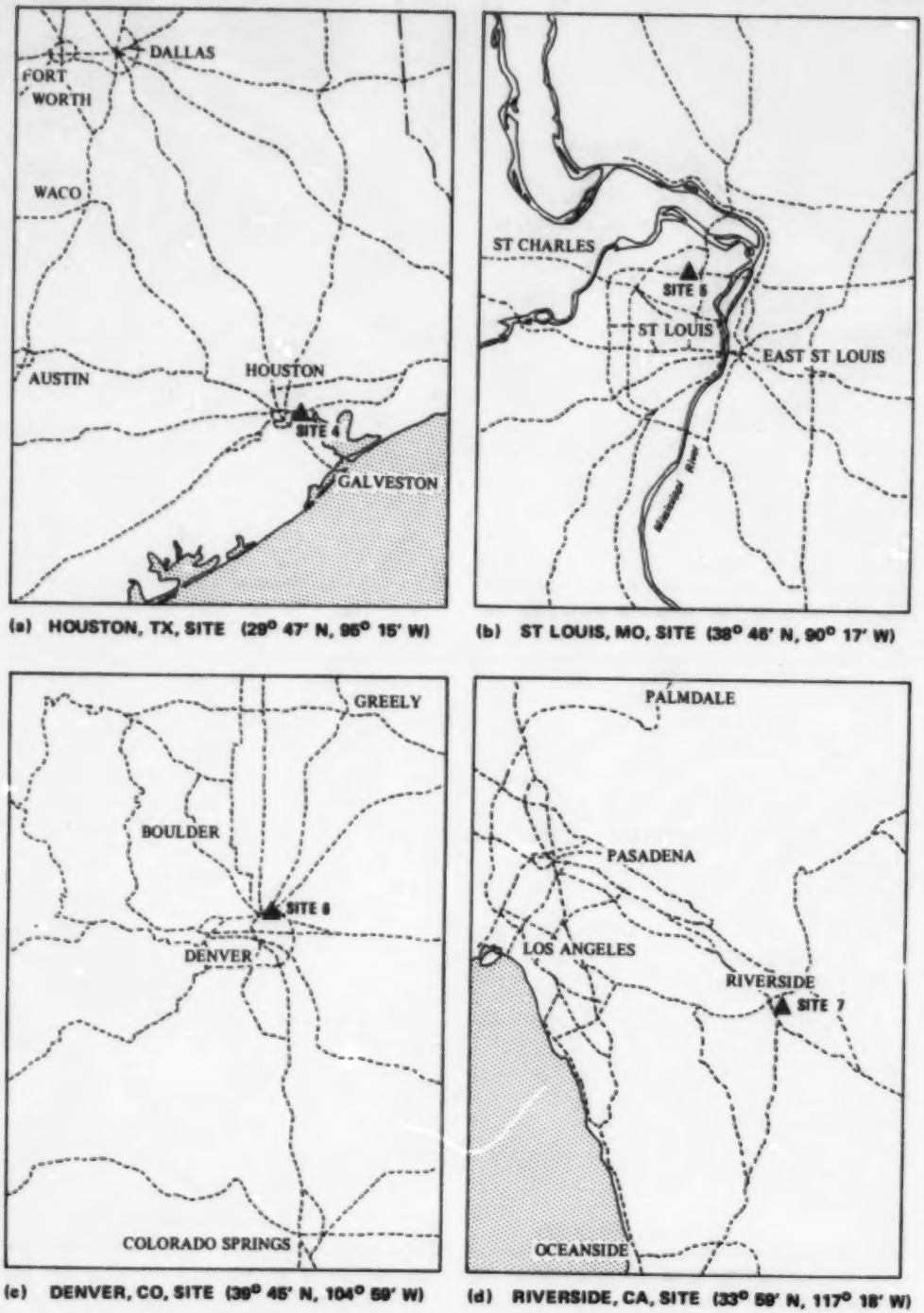

Figure 2. Location of field sites during the second year.

SECTION 6

ANALYSIS OF FIELD DATA

Experiments at all sites were performed satisfactorily, and no breakdowns were encountered. The field operations were conducted around-the-clock on a seven-day-per-week basis. This allowed the collection of a large body of data. The entire data base was collected, validated, and compiled on our master data file. This file also contains the data that were collected in the first year of this research effort. All of the meteorological information is currently on chart papers and is easily accessible. The toxic-chemical master data file will be updated as additional studies are conducted. We have compiled, validated, and statistically treated the collected data, but no detailed meteorological analyses of these data have been conducted. The interpretation of data is therefore by no means complete, and further analysis and interpretations will continue.

ATMOSPHERIC ABUNDANCES, DAILY EXPOSURES*, FATES, AND VARIABILITIES OF MEASURED SPECIES

Table 9 summarizes data on all of the organic chemicals measured during the four field studies; maximum, minimum, and average concentrations are presented for each of the measured species. The averages and the standard deviations associated with the concentration data are calculated from the actual data acquired and involve no interpolations. In addition, Table 9 presents an average daily outdoor dose for each of the species and the standard deviations associated with this average daily dose. The dose is determined based on an average daily air intake of 23 m^3 at 25°C and 1 atmosphere for a 70-kg male. The daily doses were calculated by estimating hourly values by linear interpolations between measured data. The reported-dose data in Table 9 represent the average of daily average doses and the standard deviations associated with variabilities in the daily means.

Much of the information presented in Table 9 is self-explanatory, so only salient observations will be made below. Table 10 (presented earlier as Table 2) summarizes the total average exposure for the four sites to each chemical category as defined in Table 9.

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*The terms "daily exposure" and daily dosage" are used interchangeably and do not include the efficiency of chemical absorption in the human body.

TABLE 8 CONCENTRATIONS AND DAILY OUTDOOR EXPOSURES OF MEASURED CHEMICAL SPECIES

Chemical Group and Species	Houston – Site 4 (14–25 May 1980)						St. Louis – Site 5 (29 May–6 Jun 1980)						Denver – Site 6 (15–26 Jun 1980)						Riverside – Site 7 (1–13 July 1980)					
	Concentration (ppt)				Daily Exposure* (µg/day)		Concentration (ppt)				Daily Exposure (µg/day)		Concentration (ppt)				Daily Exposure (µg/day)		Concentration (ppt)				Daily Exposure (µg/day)	
	Mean	S.D.†	Max.	Min.	Average	S.D.	Mean	S.D.	Max.	Min.	Average	S.D.	Mean	S.D.	Max.	Min.	Average	S.D.	Mean	S.D.	Max.	Min.	Average	S.D.
Chlorofluorocarbons																								
Trichlorofluoromethane (F11)	474	178	1105	305	98.6	11.5	374	105	905	217	46.8	7.1	637	255	1240	289	82.2	16.2	671	318	1680	281	97.8	19.9
Dichlorofluoromethane (F12)	887	474	2817	482	103.5	30.2	622	182	1156	383	68.7	12.5	1005	565	3178	471	107.9	24.5	1090	401	2804	667	125.2	39.0
Trichlorotrifluoroethane (F113)	199	190	1604	37	37.7	26.5	132	171	1791	22	21.9	5.1	221	235	1808	26	45.0	21.3	274	262	2211	28	44.8	11.8
Dichlorotetrafluoroethane (F114)	28	10	58	12	4.5	0.9	26	6	37	13	4.0	0.5	34	9	60	17	5.5	0.8	39	9	62	13	4.6	1.0
Halomethanes																								
Methyl chloride	965	403	2264	531	48.5	16.3	723	138	1015	531	34.1	1.2	763	132	1157	519	36.0	4.8	703	179	1193	437	34.8	8.3
Methyl bromide	100	58	378	45	9.3	3.3	81	26	126	7	7.2	1.2	124	51	227	23	11.2	3.4	259	167	1033	43	23.5	12.3
Methyl iodide	3.6	2.3	11.2	0.6	0.4	0.2	2.6	1.6	7.7	0.2	0.4	0.2	1.8	1.0	4.8	0.6	0.2	0.1	2.8	1.2	6.2	0.6	0.4	0.2
Methylene chloride	574	553	3404	49	43.0	24.6	421	583	6402	82	29.3	10.5	967	926	4874	108	76.1	34.6	1949	1406	9428	478	158.1	53.7
Chloroform	423	149	1112	38	42.8	34.6	73	30	191	25	7.9	1.8	185	205	1038	19	18.8	9.2	703	199	1747	109	76.1	44.3
Carbon tetrachloride	404	419	2934	126	61.8	43.3	129	6	148	112	18.5	0.9	174	19	274	116	25.2	1.4	175	23	267	151	25.2	1.6
Haloethanes and halopropanes																								
Ethyl chloride	227	273	1348	16	13.5	8.0	46	29	182	10	2.7	1.1	41	24	125	10	2.4	0.8	87	65	312	16	5.1	1.9
1,1 Dichloroethane	63	20	126	9	6.1	1.1	60	14	105	26	5.6	0.9	85	31	142	11	6.3	1.6	86	22	147	8	6.1	1.1
1,2 Dichloroethane	1512	1863	7300	50	125.0	81.1	124	101	607	45	11.4	4.7	241	297	2089	54	20.3	8.6	357	325	2505	63	31.8	12.3
1,2 Dibromoethane	58	72	368	10	9.8	5.6	16	4	26	8	2.8	0.4	31	15	78	10	5.5	0.9	22	7	47	10	3.9	0.5
1,1,1 Trichloroethane	353	263	1499	134	41.5	17.8	236	136	896	132	26.0	7.1	713	553	2699	171	92.3	31.2	747	257	1348	356	82.6	17.8
1,1,2 Trichloroethane	32	24	129	<5	3.1	1.8	15	6	45	6	1.9	0.4	27	10	58	7	3.4	0.6	41	21	88	<5	6.0	2.1
1,1,1,2 Tetrachloroethane	12	15	60	2	1.1	0.8	6	3	16	4	0.3	0.3	10	12	60	5	0.9	0.9	9	3	16	4	1.1	0.3
1,1,2,2 Tetrachloroethane	11	9	77	2	1.6	0.7	6	2	12	4	0.3	0.2	10	3	17	3	0.8	0.3	12	9	77	5	1.4	0.3
1,2 Dichloropropane	61	37	253	22	8.5	1.4	53	12	89	22	5.6	0.7	48	14	99	20	5.2	1.2	57	15	86	11	8.0	1.0
Chloroalkenes																								
Vinylidene chloride	25	36	136	<4	1.4	1.1	9	5	34	<4	0.4	0.2	31	49	224	<4	1.4	3.3	9	6	58	<4	0.5	0.3
(cis) 1,2 Dichloroethylene	71	50	429	21	6.3	2.6	39	8	66	25	3.5	0.5	78	61	605	25	7.3	2.4	80	14	173	33	6.4	0.5
Trichloroethylene	144	195	980	5	16.2	10.6	112	154	1040	8	13.5	7.4	198	313	2483	7	23.4	31.2	118	85	238	15	14.5	3.2
Tetrachloroethylene	401	598	3215	34	61.4	61.9	326	955	7604	67	58.4	72.9	394	188	1130	89	59.5	11.4	484	236	1529	173	76.7	20.8
Allyl chloride	<5	–	<5	<5	<0.4	–	<5	–	<5	<5	<0.4	–	<5	–	<5	<5	<0.4	–	<5	–	<5	<5	<0.4	–
Hexachloro 1,3 butadiene	11	20	164	1	2.7	2.7	3	2	10	1	0.7	0.2	2	1	7	0.4	0.5	0.2	4	3	16	1	1.1	0.3
Chloroaromatics																								
Monochlorobenzene	309	517	2785	9	34.4	34.8	240	243	1167	5	23.6	10.3	260	217	1114	33	27.0	12.4	–	–	–	–	–	–
o-Chlorotoluene	<5	–	58	<5	<0.6	–	<5	–	26	<5	<0.6	–	<5	–	111	<5	<0.6	–	<5	–	39	<5	<0.6	–
o-Dichlorobenzene	7	9	67	1	1.0	0.7	6	11	85	1	0.8	0.6	26	34	227	2	4.3	2.9	10	8	76	3	1.4	0.4
m-Dichlorobenzene	7	8	47	1	0.7	0.3	4	8	55	1	0.3	0.3	8	7	36	1	1.0	0.6	6	4	21	1	0.6	0.3
p-Dichlorobenzene	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
1,2,4 Trichlorobenzene	2	2	13	1	0.4	0.1	1	1	4	1	0.2	0.0	6	4	35	1	1.0	0.9	10	7	40	2	1.7	0.3
Aromatic hydrocarbons																								
Benzene	5780	5880	37700	840	449.2	283.3	1410	1190	5820	110	91.0	48.4	4340	3940	23810	110	302.4	139.9	3950	1910	10880	529	389.4	63.9
Toluene	10330	10950	65650	1040	822.4	419.9	1520	1250	6450	103	126.0	64.9	6240	5280	24680	290	511.6	173.1	6800	3670	20870	450	698.9	158.8
Ethyl benzene	1380	1400	7280	50	136.7	84.8	640	480	2100	50	44.9	23.9	2720	3130	18130	90	195.5	84.8	1330	620	4000	250	127.7	30.9
m-/p-Xylene	3840	4270	23760	270	362.1	218.4	950	703	3230	110	86.8	50.9	2960	3320	20850	150	263.3	139.6	2231	1515	7340	280	215.5	52.9
o-Xylene	1307	1480	8790	80	123.7	65.8	310	300	1490	60	21.9	11.0	1280	1210	6000	< 10	112.7	50.9	1100	650	3140	80	102.7	22.9
4-Ethyl toluene	870	1030	7470	60	90.3	44.0	240	180	1240	80	10.2	11.3	900	780	4380	70	88.1	31.6	820	480	2650	70	85.8	22.6
1,2,4 Trimethyl benzene	1160	1470	8260	50	118.6	54.7	370	370	2560	60	12.4	26.0	1410	2310	15450	130	122.0	74.5	740	500	3130	100	76.4	50.7
1,3,5 Trimethyl benzene	460	800	5350	70	27.1	21.5	530	490	1360	80	26.2	13.6	340	240	1260	30	30.3	11.3	330	170	1260	70	13.6	9.6
																			> 50					
Oxygenated species																								
Formaldehyde	–	–	–	–	–	–	11300	4500	18700	6160	318.0	127.0	12300	5800	28700	6900	347.0	167.0	19000	7600	41000	10400	536.0	216.0
Phosgene	< 20	–	< 20	–	< 1	–	< 20	–	< 20	–	< 1	–	< 20	–	< 20	–	< 1	–	> 50	–	–	–	> 2.5	–
Peroxyacetylnitrate (PAN)	438	835	4350	< 10	44.0	45.4	277	203	890	40	24.4	8.0	443	1248	11847	12	45.0	21.4	1196	1249	5780	120	136.8	40.8
Peroxypropionylnitrate (PPN)	110	140	630	< 10	6.5	6.0	64	93	250	< 10	0.5	1.2	45	47	318	< 10	4.4	2.7	193	197	900	< 10	19.2	8.3

*Daily average exposure based on total air intake of 23 m^3/day at 25°C and 1 atm pressure

†Standard deviation

TABLE 10. SUMMARY OF EXPOSURE TO HAZARDOUS ORGANIC CHEMICAL GROUPS

Chemical Category*	Total Average Daily Exposure (μg/day)				
	Houston – Site 4	St. Louis – Site 5	Denver – Site 6	Riverside – Site 7	Average of Sites
Chlorofluorocarbons†	205	141	241	262	212
Halomethanes	203	97	168	319	197
Haloethanes and halopropanes	210	59	137	153	140
Chloroalkenes	88	78	92	98	89
Chloroaromatics	37	25	34	–	32
Aromatic hydrocarbons	2130	430	1616	1401	1394
Oxygenated species	–	344	396	696	479

*As defined in Table 9

†NOT suspected to be directly toxic

DATA ANALYSIS BY CHEMICAL CATEGORY

Chlorofluorocarbons (CFCs)

Four CFCs (fluorocarbon 11, 12, 113 and 114) were measured. As indicated earlier (Table 3), CFCs are not expected to be toxic to the human body. They do, however, act as useful indicators of urban transport, and the involvement of these halocarbons in stratospheric ozone destruction is well known. It is clear from Table 9 that the mean F12:F11 ratio at Site 4 is 1.9, while this ratio is between 1.6 and 1.7 for the other sites. While emissions information for F12 and F11 for 1980 is not available, an F12:F11 ratio of 1.6 to 1.7 is consistent with cumulative emission rates. The Houston ratio is slightly higher but probably reflects a greater use of air-conditioned automobiles that use F12 as a refrigerant. The consistency in data is much less obvious when one considers the F12:F113 ratios: this ratio varied between 3 and 5 at all of the sites. Past emission ratios would suggest that this ratio should be greater than 10. To the extent that urban data can act as an early warning indicator of major changes in use patterns, it would seem that emissions of F113 are increasing at a faster rate than all other fluorocarbons. Since F113 is comparable to F11 in its stratospheric-ozone-destroying efficiency, its use should be watched more carefully. The F114 levels are reasonable and not inconsistent with available emissions data.

Halomethanes

Six halomethanes were measured. As can be seen from Table 3, all six of these chemicals are either mutagens or suspected carcinogens. It should be pointed out that methyl chloride, one of the most dominant natural chlorine carriers, is also found to be mutagenic in the salmonella mutagenicity tests. Methyl bromide and methylene chloride are also mutagens (Table 3). The total intake of halomethanes varies between 100 and 300 μg/day, depending upon the city and the prevailing weather conditions (Table 10).

Average methyl chloride levels were typically less than 1 ppb. Measured levels of approximately 700 parts per trillion (ppt) at Sites 5, 6, and 7 are only slightly elevated above the expected background (≃ 600 parts per trillion). However, the variability in methyl chloride levels at Site 4 (Houston) was significant. Figure 3(a), (b), and (c) best demonstrates the selective sources of methyl chloride. While general meteorological conditions at St. Louis did not allow for much pollution, this was not the case at Riverside. Days 6 through 10 at Riverside were extremely polluted (as shall be seen later) and yet little variability in methyl chloride was found. From Figure 3, one can conclude that methyl chloride may be found significantly above background levels only in some urban centers.

The behavior of methyl bromide was more typical of an urban pollutant. It is safe to assume that in most polluted environments methyl bromide levels are significantly above the expected background of about 10 to 15 parts per trillion. The unusually high levels measured in Riverside (average of 0.26 ppb) are consistent with similarly high values reported previously for the nearby city of Los Angeles (Singh et al., 1979). Figure 4 clearly shows the variability in methyl bromide levels that is consistent with other anthropogenic pollutants (e.g. methylene chloride).

Methyl iodide was carefully measured to avoid any possible interferences from other pollutants. It was resolved on two different GC columns: The results were essentially identical. Average methyl iodide levels were between 2 and 4 parts per trillion at all sites. At no time did the concentration exceed 11 parts per trillion. Methyl iodide is a suspected carcinogen (Table 3), and yet it is a component of the natural atmosphere. Typical levels of 4 to 6 parts per trillion are encountered in the marine environments. It appears that methyl iodide has no sources in the urban environment. Figure 5 shows a mild diurnal variation in methyl iodide with a slight dip in the afternoon levels.

Methylene chloride is clearly a large volume organic chemical (concentrations reached as high as 9 ppb). At all sites the average concentration exceeded 0.4 ppb, and the concentration was highest in Riverside (average = 1.9 ppb). This is somewhat lower than the average concentration of 3.8 ppb measured in central Los Angeles (Singh et al., 1979). The diurnal behavior of methylene chloride at Houston and Denver [Figure 6(a) and (b)] was somewhat similar and showed reduced levels in the afternoon. This is contrary to the behavior observed at Riverside where a distinct afternoon maximum is observed [Figure 6(c)]. This is in part attributable to the downwind location of Riverside, which is subject to transport from Los Angeles. Figure 7 clearly

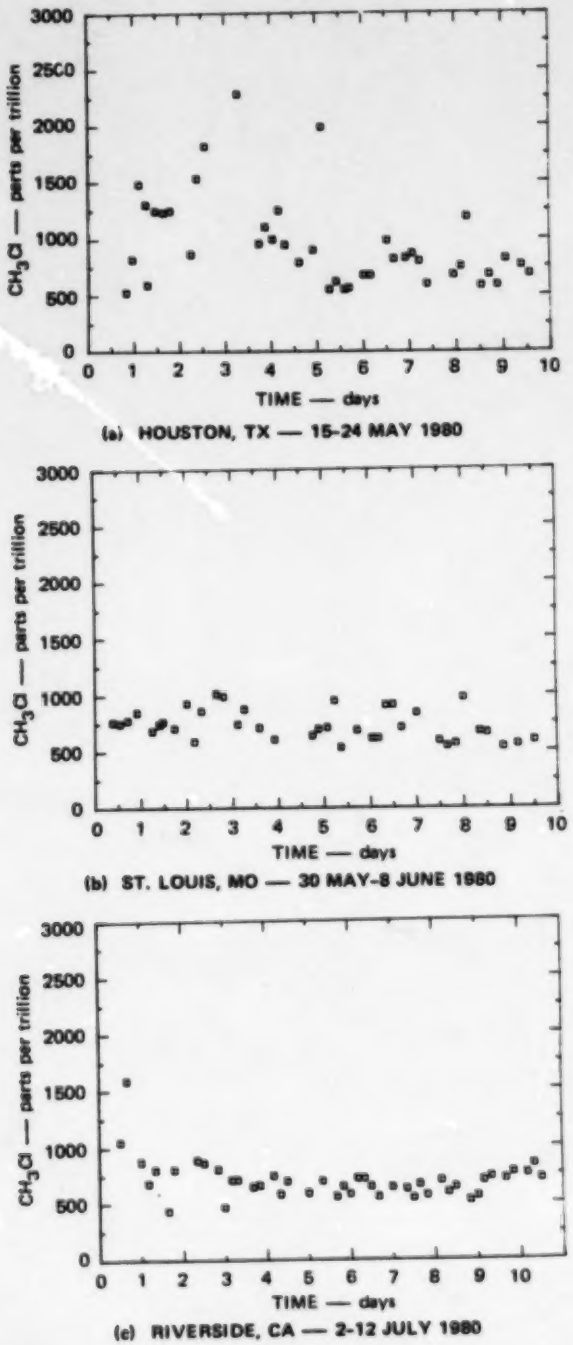


Figure 3. Atmospheric concentration of methyl chloride.

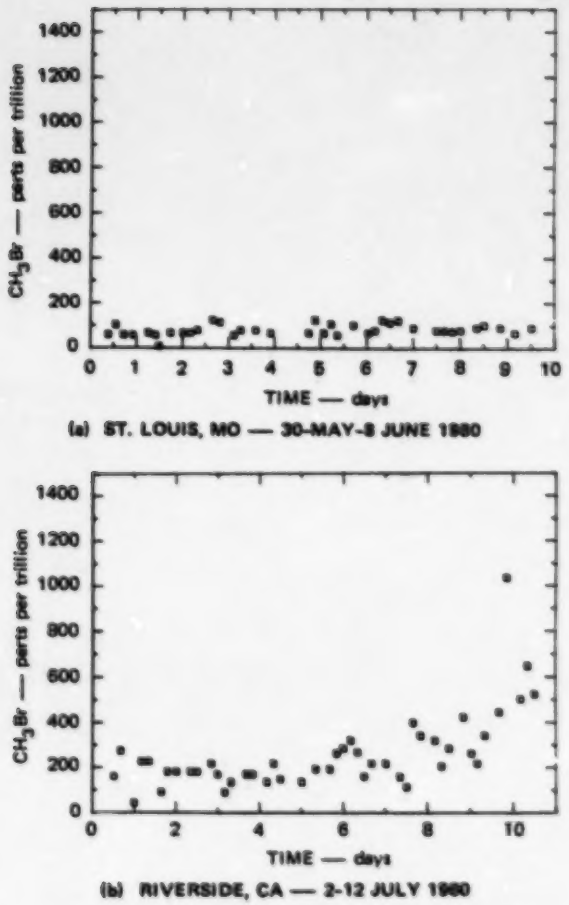


Figure 4. Atmospheric concentration of methyl bromide.

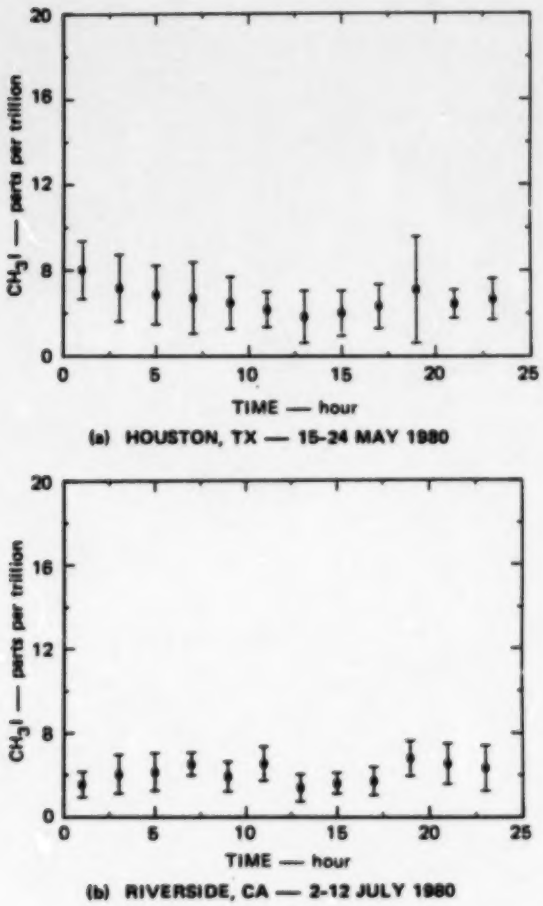


Figure 5. Mean diurnal variation of methyl iodide.

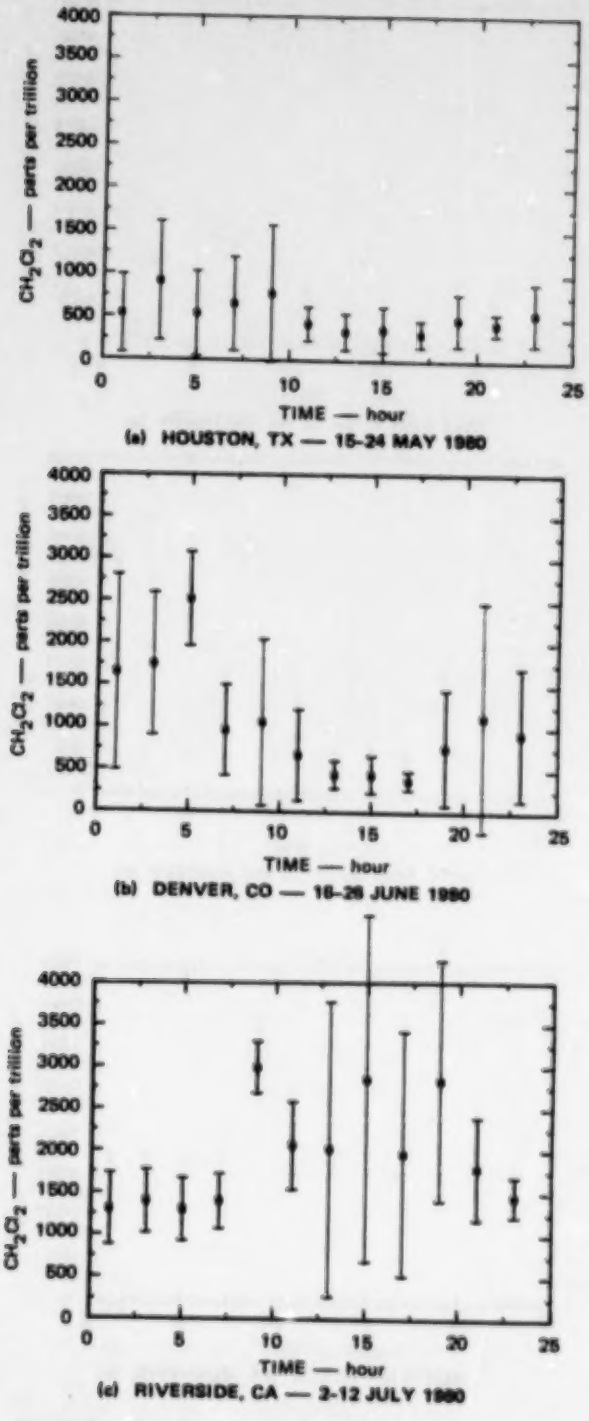


Figure 6. Mean diurnal variation of methylene chloride.

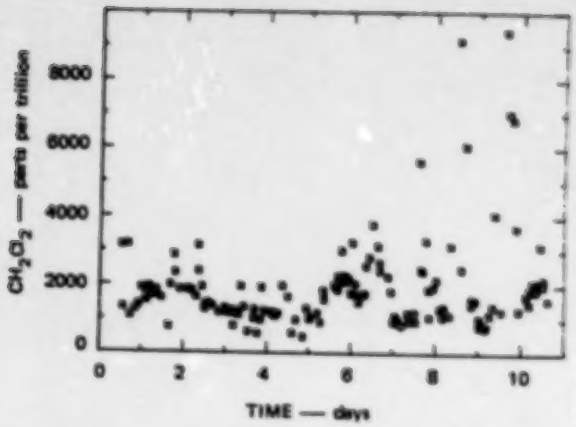


Figure 7. Atmospheric concentration of methylene chloride at Riverside, CA, 2-12 July 1980.

shows the observation made earlier that the last half of our stay at Riverside showed significantly greater pollution than the first half. The average intake of methylene chloride varied from 30 to 160 µg/day at all sites.

Chloroform levels are significantly elevated in the urban environments. Concentrations approaching 5 ppb were encountered at more than one site. The average daily intake of chloroform was as low as 9 µg/day in St. Louis and was close to 80 µg/day in Riverside (Table 9). The sources of cloroform are still largely unknown but automobiles, chlorination of water, and direct emissions probably all contribute significantly. The variability of chloroform at Riverside is nearly identical to methylene chloride (Figures 7 and 8), further confirming its urban source.

Unlike most other man-made pollutants, carbon tetrachloride showed little variability at all sites except at Houston. This is clearly shown in Figure 9. The lack of variability of carbon tetrachloride at Riverside is intriguing. Carbon tetrachloride levels as high as 3 ppb were encountered (Table 9). The average daily intake at all sites was typically between 18 and 25 µg/day except in Houston, where it was 62 µg/day.

Haloethanes and Halopropanes

Nine important chemicals in this category were measured (Table 9). This is the first measurement of ethyl chloride, and no comparative data are available. It is estimated that 0.01 million tons of ethyl chloride is released into the atmosphere every year in the United States. Our measurements suggested high levels of this chemical in Houston, where concentrations as high as 1.3 ppb were encountered. The average concentration (0.23 ppb) and the daily average dose (14 µg/day) were also highest in Houston (Figure 10).

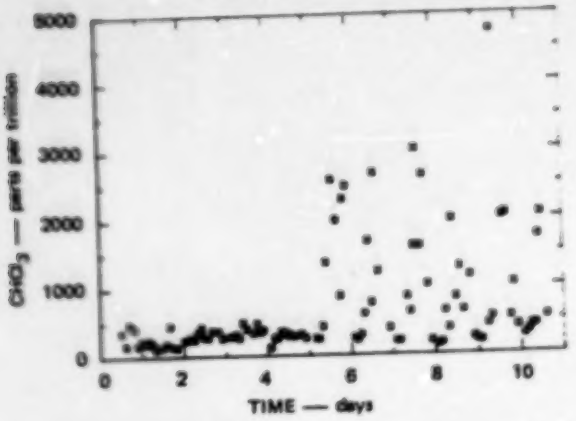
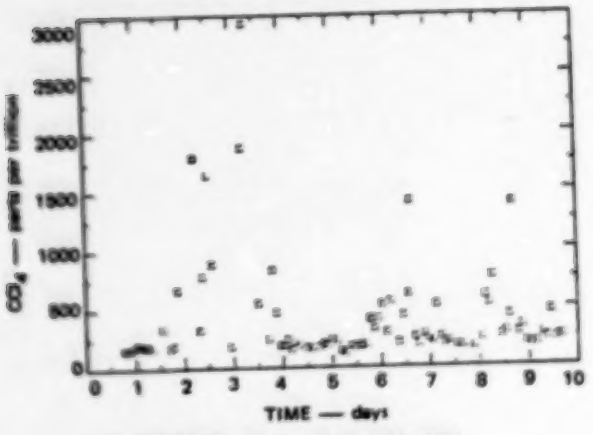
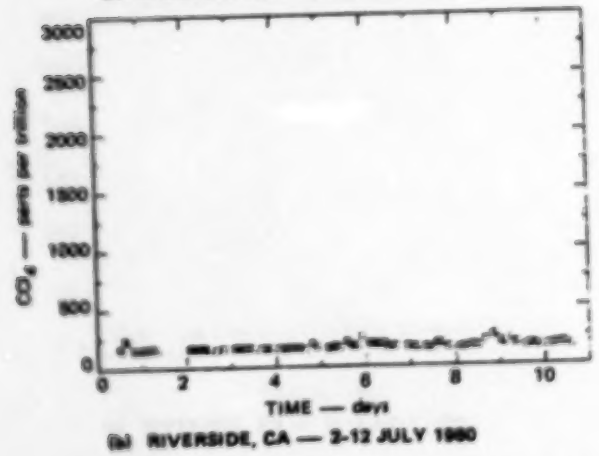


Figure 8. Atmospheric concentration of chloroform at Riverside, CA, 2-12 July 1980.



(a) HOUSTON, TX — 15-24 MAY 1980



(b) RIVERSIDE, CA — 2-12 JULY 1980

Figure 9. Atmospheric concentration of carbon tetrachloride.

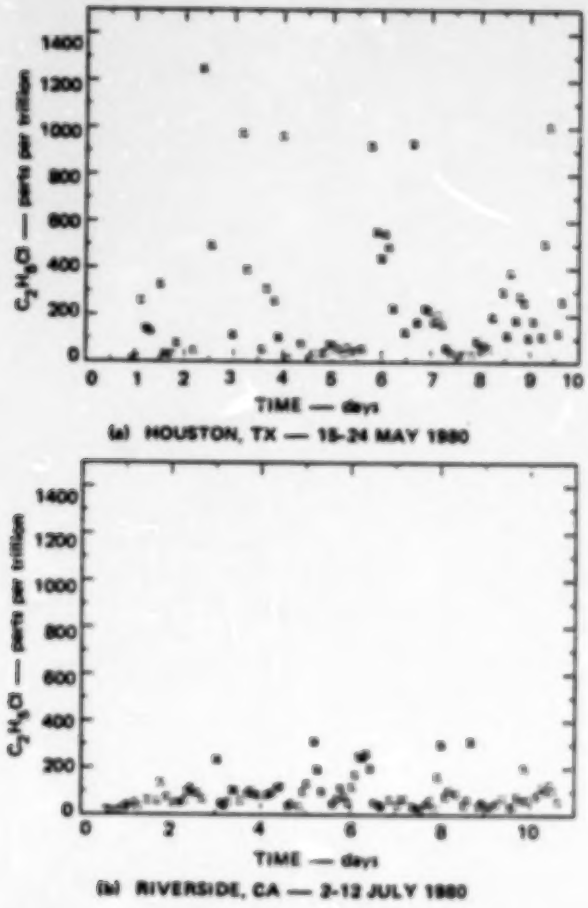


Figure 10. Atmospheric concentration of ethyl chloride.

Average levels in St. Louis, Denver, and Riverside were 0.05 ppb, 0.04 ppb, and 0.09 ppb respectively (Table 9). Typical measured levels are not inconsistent with estimated emissions. No toxicity data on ethyl chloride was available.

Unlike ethyl chloride, the variability in 1,1 dichloroethane was not large. Average concentrations were between 0.06 ppb and 0.07 ppb at all sites, and concentrations did not exceed 0.15 ppb. A daily average dose of 6 μg/day is calculated for all four sites. Based on the meteorological condition a diurnal trend was evident. Figure 11 shows this behavior at Denver (Site 6) and Riverside (Site 7). 1,1 Dichloroethane is not found to be a bacterial mutagen (Table 3).

1,2 Dichloroethane is a large-volume chemical that is also a suspected mutagen and a carcinogen (Table 3). Its estimated yearly U.S. emissions exceed 0.2 million tons. The distribution of 1,2 dichloroethane was widely different at the four sites but was highest in Houston, where concentrations as high as 7.3 ppb were measured (Figure 12). The average 1,2 dichloroethane

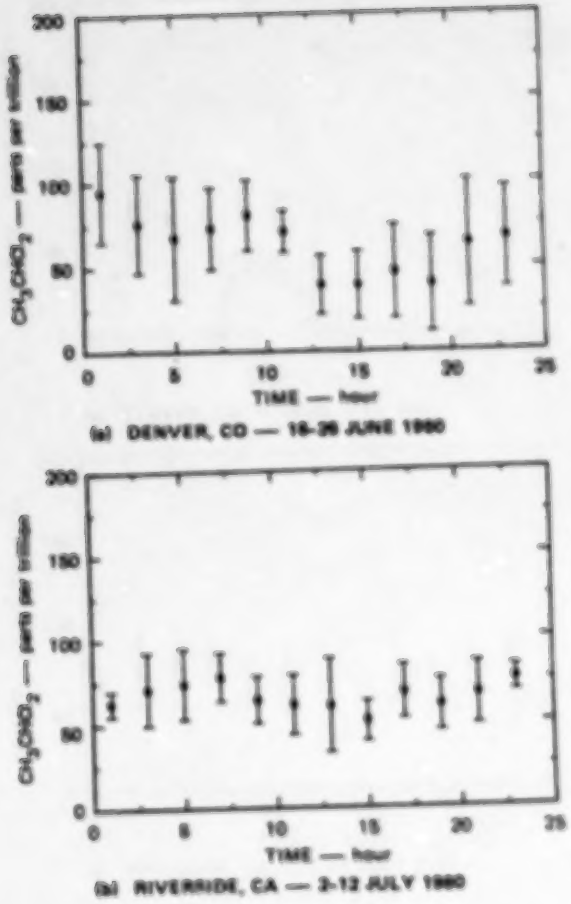


Figure 11. Mean diurnal variation of 1,1 dichloroethane.

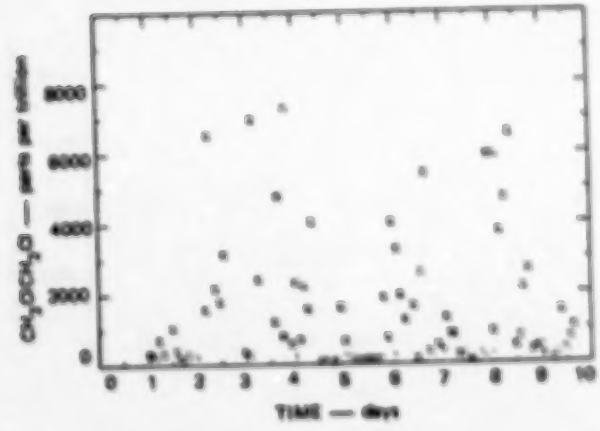


Figure 12. Atmospheric concentration of 1,2 dichloroethane.

concentration in Houston was 1.5 ppb, which was an order of magnitude higher than the lowest average measured at St. Louis (Table 9). While the diurnal variation at Houston does not follow any special trend, the diurnal trend at Denver is very much like that of 1,1 dichloroethane (Figure 13).

The high 1,2 dichloroethane concentrations in Houston were measured although the weather on several days was rainy and windy and unsuited for pollutant accumulation. During more typical (stagnant) summer weather, this site has the potential to be a toxic "hotspot." The lack of a reasonable diurnal variation of 1,2 dichloroethane at Houston is probably attributable to constantly changing weather conditions and the proximity of local sources. The lowest measured level of about 45 parts per trillion is representative of the background of 1,2 dichloroethane in the free troposphere at midlatitudes.

1,2 Dibromoethane is a suspected carcinogen (Table 3) that has a high risk associated with its exposure (Table 4). Fortunately, the levels of 1,2 dibromoethane are moderately low at all sites and the average concentration did not exceed 0.06 ppb at any of the four sites. The highest concentration of 0.37 ppb was measured at Houston. This may be partially attributed to the

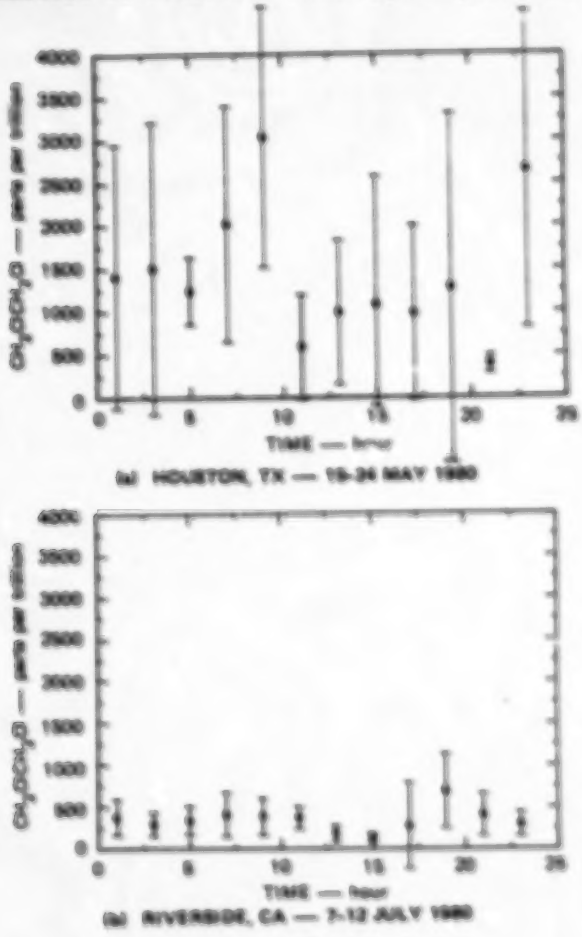


Figure 13. Mean diurnal variation of 1,2 dichloroethane.

proximity of this site to Highway 10. The average daily exposure at all sites varied between 3 and 10 μg/day. Figure 14 shows the daily variability and the mean diurnal variation of 1,2 dibromoethane at Denver (Site 7).

1,1,1 Trichloroethane is another large-volume chemical that may be a weak mutagen (Table 3). The highest concentration of 2.7 ppb was measured at Denver. The lowest levels of about 140 parts per trillion are reflective of its geochemical background. The daily average dose was determined to be 42 μg/day, 28 μg/day, 92 μg/day and 93 μg/day at Sites 4, 5, 6 and 7 respectively (Table 9). The diurnal behavior of 1,1,1 trichloroethane at three selected sites is shown in Figure 15. It is interesting that while methylene chloride shows an afternoon maximum at Riverside, 1,1,1 trichloroethane shows a minimum. This is largely due to the superimposition of afternoon vertical mixing on the downwind transport. The large concentrations of methylene chloride indicate that the reduction in species concentration caused by vertical mixing is overwhelmed by the high transport source. The diurnal variation of 1,1,2 trichloroethane is very similar to that of 1,1,1 trichloroethane (Figure 16), even though its average levels are at least an order of magnitude lower.

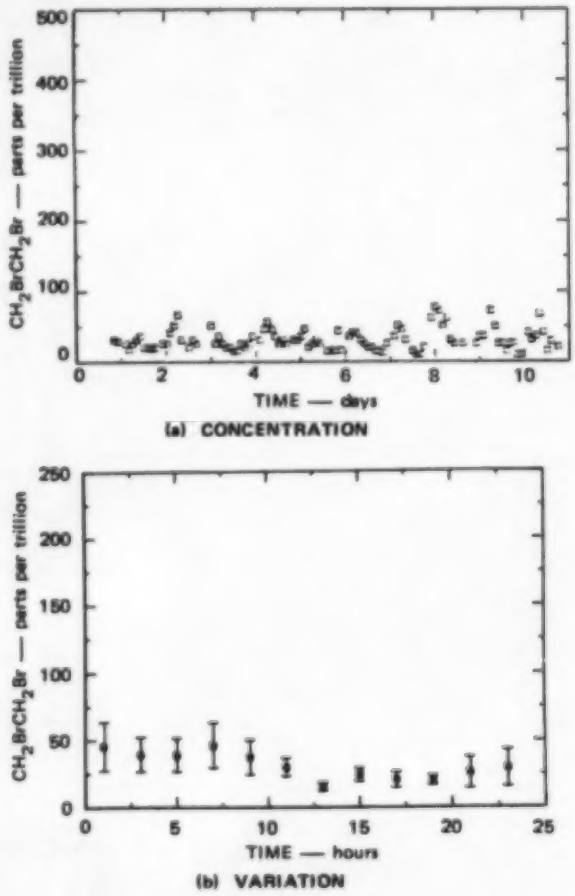


Figure 14. Atmospheric concentration and mean diurnal variation of 1,2 dibromoethane at Denver, CO, 16-26 June 1980.

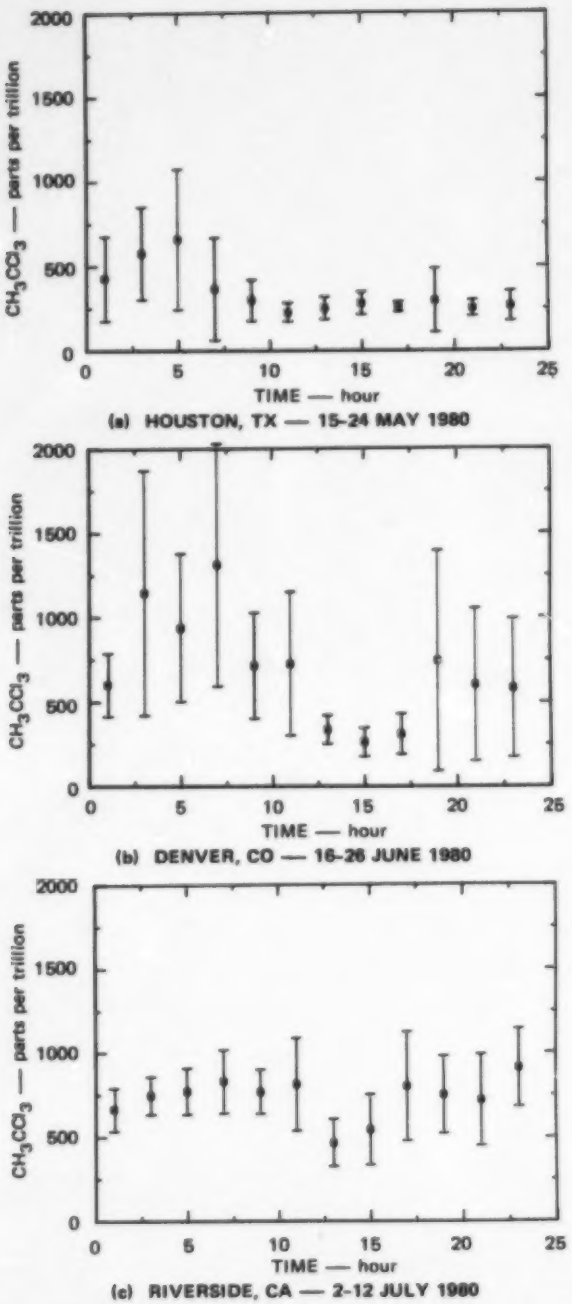


Figure 15. Mean diurnal variation of 1,1,1 trichloroethane.

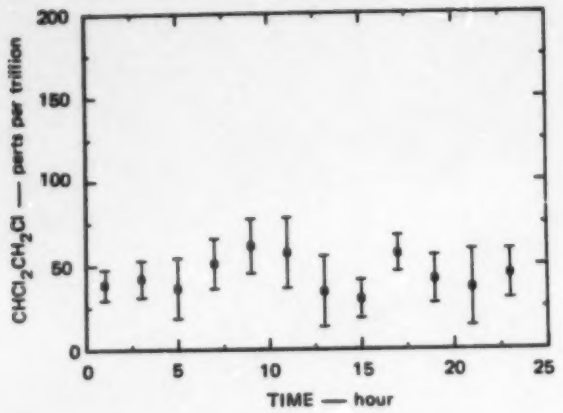


Figure 16. Mean diurnal variation of 1,1,2 trichloroethane at Riverside, CA, 2-12 July 1980.

Extremely small amounts of tetrachloroethanes were measured. The two isomers (1,1,1,2 and 1,1,2,2) together were present at an average concentration of about 20 parts per trillion (Table 9). At no time did the concentration of either one of these isomers exceed 0.1 ppb. The symmetric isomer (1,1,2,2) is found to be a bacterial mutagen and is suspected to be a carcinogen (Table 3). The asymetric isomer (1,1,1,2) has been tested for mutagenicity with negative results (Table 3).

1,2 Dichloropropane was the only chlorinated propane measured. There was also evidence of the presence of a chemical tentatively identified to be an isomer of dichloropropene, but further tests are necessary to ascertain its identity. Dichloropropane, like many of the chlorinated ethanes, is a bacterial mutagen (Table 3). Its concentrations were relatively uniform in all cities except Houston, where concentrations as high as 0.25 ppb were measured. Average concentrations were 0.08 ppb at Houston (Site 4) and between 0.05 ppb and 0.06 ppb at all other sites. Average outdoor intake is determined to be about 6 to 8 µg/day. Figure 17 shows the diurnal behavior of 1,2 dichloropropane at Riverside.

Chloroalkenes

Six chloroalkenes were sought. Of these, allyl chloride (a suspected carcinogen) was found to be present at concentrations of less than 5 parts per trillion at all sites. Vinyledene chloride (a bacterial mutagen and a suspected carcinogen) was measured at an average concentration of 10 to 30 parts per trillion at all sites. It was below our limit of sensitivity (4 parts per trillion) at approximately 30 percent of the time. The highest concentration measured was 0.23 ppb. The low abundance of vinyledene chloride is at least partially attributable to its rapid removal from the atmosphere (Sing et al.,

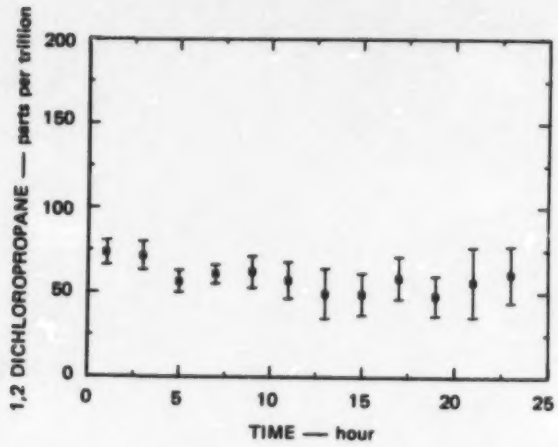


Figure 17. Mean diurnal variation of 1,2 dichloropropane at Riverside, CA, 2-12 July 1980.

1979). Another equally reactive dichloroethylene (cis-1,2) was found to be more ubiquitous. Concentrations of 1,2 dichloroethylene as high as 0.6 ppb were measured in Denver. Average concentrations at all sites varied between 40 and 80 parts per trillion. Together the two dichloroethylenes add up to a daily intake of 4 to 8 μg/day. Unlike vinyledene chloride, the symmetric isomer is not found to be a mutagen. No carcinogenicity data on 1,2 dichloroethylene are currently available (Table 3).

One of the two dominant chloroethylenes in the atmosphere is trichloroethylene. It is a large-volume chemical (annual U.S. emissions = 0.15 million tons) that is also a suspected carcinogen. The highest concentration of 2.5 ppb was measured at Denver (Table 9). The average concentrations were typically between 0.1 to 0.2 ppb. The atmospheric variability of trichloroethylene is substantial and is due to both variable emissions and a very short atmospheric lifetime (Singh et al., 1979). The diurnal behavior of trichloroethylene at Sites 4, 6, and 7 is shown in Figure 18. The daily average outdoor intake is determined to lie between 15 μg/day and 25 μg/day.

The second large-volume chloroethylene that is also a suspected carcinogen is tetrachloroethylene. Its annual U.S. emissions are estimated to be about 0.3 million tons. At all sites the tetrachloroethylene atmospheric abundance was 2 to 4 times that of trichloroethylene. This is due to larger emissions as well as its much longer lifetime when compared to trichloroethylene (Singh et al., 1979). The highest concentration of tetrachloroethylene was 7.6 ppb. The daily average dose was determined to be between 60 and 80 μg/day at all sites. The diurnal behavior of tetrachloroethylene was similar to trichloroethylene (Figure 19).

The sources of hexachloro-1,3 butadiene (HCBD) are secondary, since its production appears to have stopped in the mid 1960s. It has also been

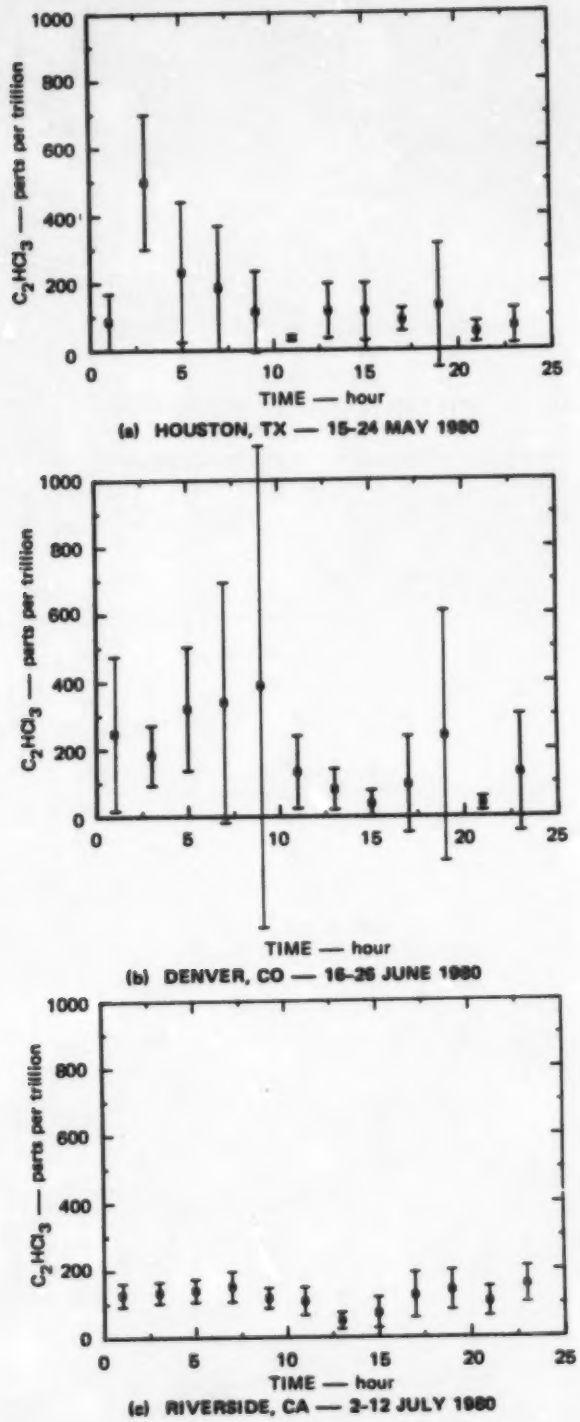


Figure 18. Mean diurnal variation of trichloroethylene.

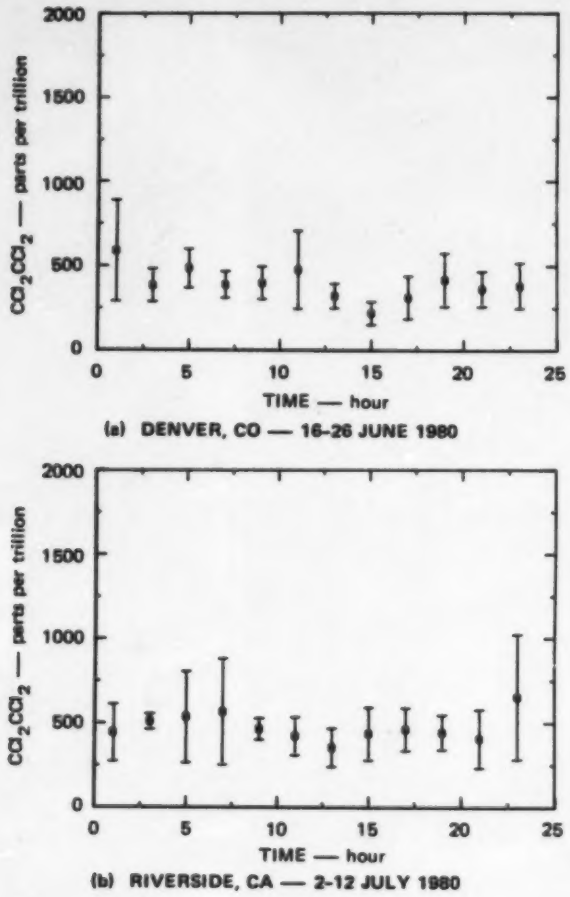


Figure 19. Mean diurnal variation of tetrachloroethylene.

identified in the effluents of sewage treatment plants. Recognized to be a bacterial mutagen (Table 3), its average atmospheric abundance is quite low (2 to 10 parts per trillion). The daily average dose is estimated to be between 0.5 and 3 μg/day. No information is available on the reactivity of HCBD, but its chemical structure would suggest that it is unlikely to be completely inert.

Chloroaromatics

Six chloroaromatics were sought. No data are being reported of p-dichlorobenzene because of unknown interferences. Monochlorobenzene was the most dominant of the chlorobenzenes and its average concentration appeared to be close to 0.3 ppb. The highest concentration was 2.8 ppb in Houston. This is not inconsistent with its large source (0.1 to 0.15 million tons/year in the United States) and its moderately long lifetime. Figure 20 shows the diurnal variation of monochlorobenzene, which is typical of other species at this site including m-dichlorobenzene (Figure 21). Both dichlorobenzenes (m- and o-) together were present at an average concentration of 15 to 30

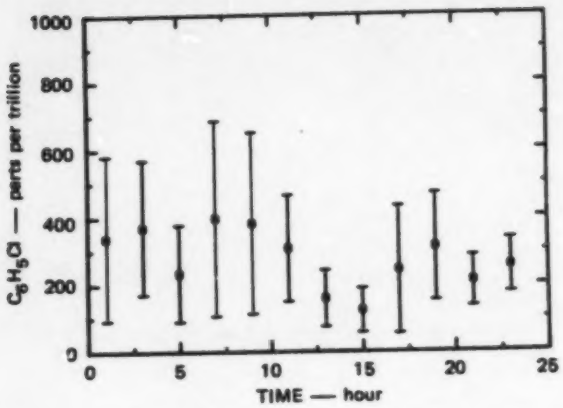


Figure 20. Mean diurnal variation of monochlorobenzene at Denver, CO, 16-26 June 1980.

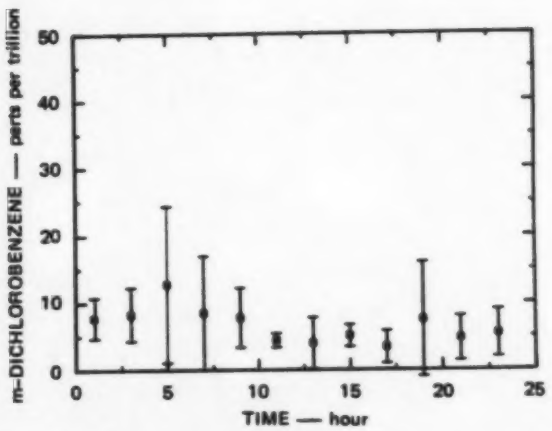


Figure 21. Mean diurnal variation of m-dichlorobenzene at Denver CO, 16-26 June 1980.

parts per trillion at all sites. Typically o-dichlorobenzene was somewhat more abundant than m-dichlorobenzene. The highest measured concentrations of o- and m-isomers were 0.23 ppb and 0.05 ppb respectively. 1,2,4 Trichlorobenzene was ubiquitously present, but its concentration never exceeded 0.04 ppb. Average intake was always less than 2 μg/day. Figure 22 shows the diurnal behavior of 1,2,4 trichlorobenzene (TCB) at Riverside. The diurnal pattern was typical of other pollutants at this site. Toxicity data are not available for most chlorobenzenes. α-chlorotoluene, a suspected mutagen, was also sought but was found to be present at average concentrations that were less than 5 parts per trillion. Excursions in α-chlorotoluene were encountered, and levels as high as 0.1 ppb were measured. Given the very low emission rate of α-chlorotoluene ($\simeq$ 0.5 thousand tons per year in the United States) its absence from the ambient atmosphere at average levels above 5 parts per trillion is not surprising.

Aromatic Hydrocarbons

Eight aromatic hydrocarbons were sought. While benzene is suspected to be carcinogenic (Table 3), the carcinogenicity of other aromatic hydrocarbons is currently uncertain. The two most dominant aromatic hydrocarbons were benzene and toluene. The average abundance of toluene exceeded that of benzene at all sites: Average toluene/benzene concentration ratios at Sites 4, 5, 6, and 7 were respectively 1.8, 1.1, 1.4, and 1.5. As the air masses aged (or in cleaner environments) the toluene/benzene ratio decreases, largely because of the longer lifetime of benzene compared to toluene (8 days versus 2 days). Highest benzene and toluene concentrations of 38 ppb and 66 ppb were measured in Houston. Benzene average intake at Houston was 450 μg/day and 91 μg/day at St. Louis. The toluene intake was correspondingly higher (Table 9).

A common source of all measured aromatic hydrocarbons was indicated, as the diurnal variation of all the aromatic hydrocarbons at a given site

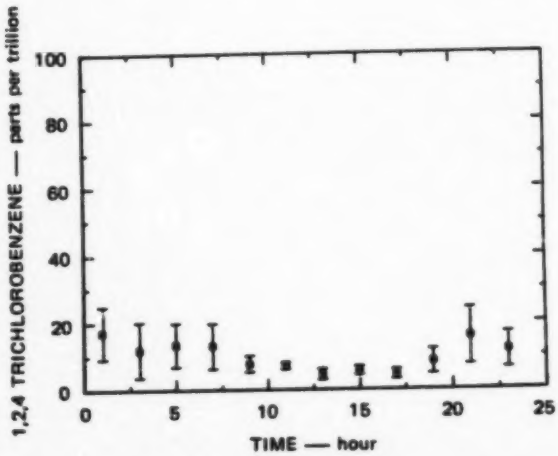


Figure 22. Mean diurnal variation of 1,2,4 trichlorobenzene at Riverside, CA, 2-12 July 1980.

was nearly identical. Figures 23 and 24 clearly show the nearly identical diurnal behavior of benzene and toluene at individual sites. Figure 25 demonstrates that other aromatic hydrocarbons also showed virtually identical diurnal behavior.

As a whole, the aromatic hydrocarbon group is the most dominant, and daily intake of this group was the highest at all sites (Table 10).

Oxygenated Species

Four oxygenated species were sought: formaldehyde, phosgene, peroxyacetyl nitrate (PAN), and peroxypropionyl nitrate (PPN). Liquid chromatographic analysis of other aldehydes that are also toxic is currently underway. Formaldehyde, a suspect carcinogen (Table 3), was measured at relatively high concentrations that varied from 6 to 41 ppb. The abundance of formaldehyde compared to most other carcinogens that were measured in urban atmospheres is significant. It is also found to be a bacterial mutagen and a suspected carcinogen (Tables 3 and 4). Figure 26 plots the formaldehyde concentration data obtained at Sites 5, 6, and 7. No clear diurnal trends are apparent. At Riverside (Site 7) an afternoon maximum is evident. The daily dose of formaldehyde at Sites 5, 6, and 7 is determined to be 319 μg day, 347 μg/day, and 536 μg/day, respectively, which is higher than the daily dose of benzene at these sites.

Phosgene was not detected at most sites, largely because the coulometer also was used for analysis of PAN, and PPN. Rain at Houston and St. Louis prevented the formation and accumulation of phosgene. Limited data from Riverside suggests levels approaching 50 parts per trillion (still very low).

As is clear from Table 9, PAN and PPN levels were quite low at all sites. This is largely attributable to the prevailing weather. Maximum PAN levels at sites 4, 5, 6, and 7 were 4.4 ppb, 0.9 ppb, 11.5 ppb, and 5.6 ppb. The PPN levels were roughly lower by a factor of 5 when compared to those of PAN. Also, PPN was less than 10 parts per trillion a significant (30 to 50 percent) fraction of the time. The diurnal variation of PAN shown in Figure 27 for Riverside is somewhat typical of that area. It is pertinent to repeat here that coulometric analysis was used for PAN and PPN determination: The quantitative nature of the coulometric response of PAN and PPN has not been tested.

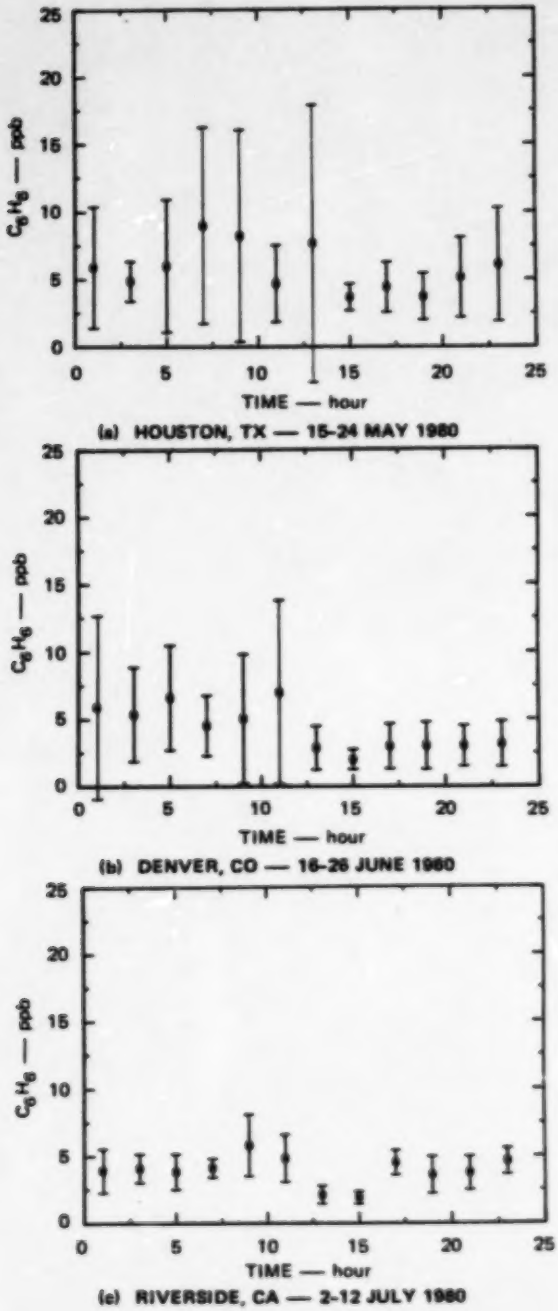


Figure 23. Mean diurnal variation of benzene.

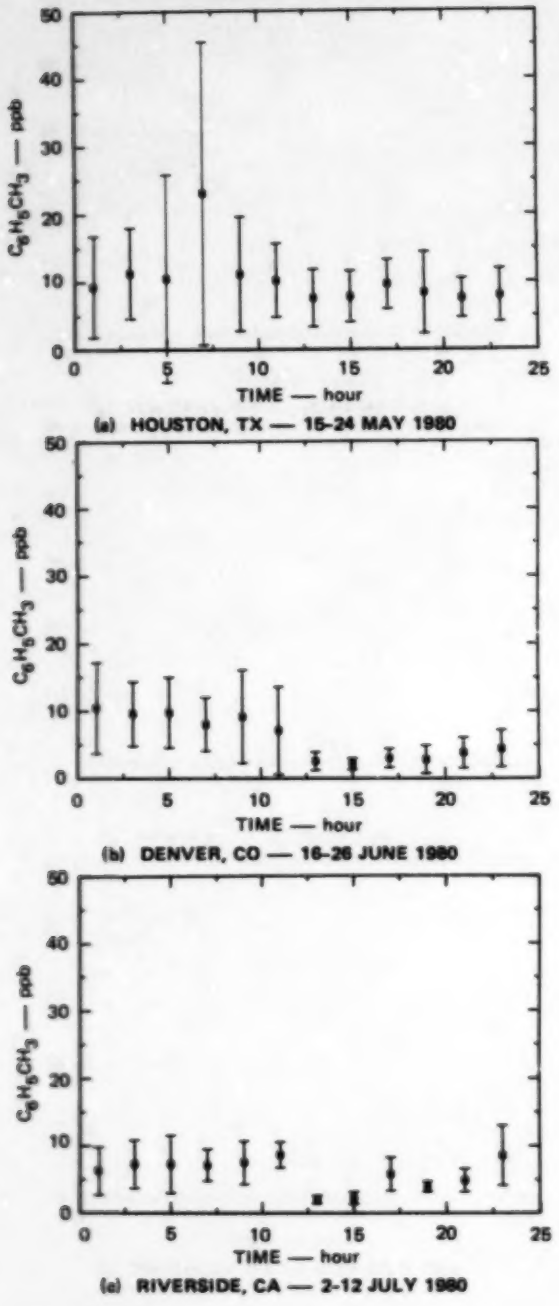

$C_6H_5CH_3$ — ppb
TIME — hour
(a) HOUSTON, TX — 15-24 MAY 1980
$C_6H_5CH_3$ — ppb
TIME — hour
(b) DENVER, CO — 16-26 JUNE 1980
$C_6H_5CH_3$ — ppb
TIME — hour
(c) RIVERSIDE, CA — 2-12 JULY 1980

Figure 24. Mean diurnal variation of toluene.

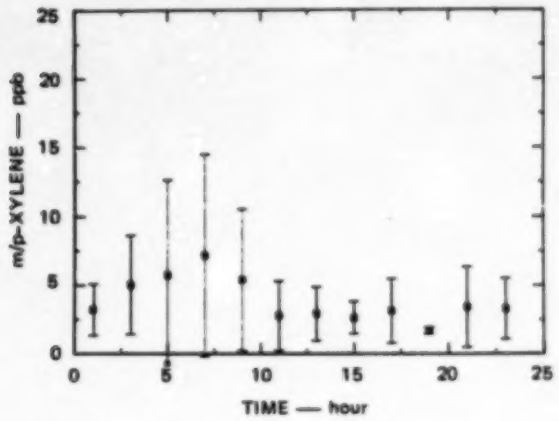


Figure 25. Mean diurnal variation of m/p-xylene at Houston, TX, 15-24 May 1980.

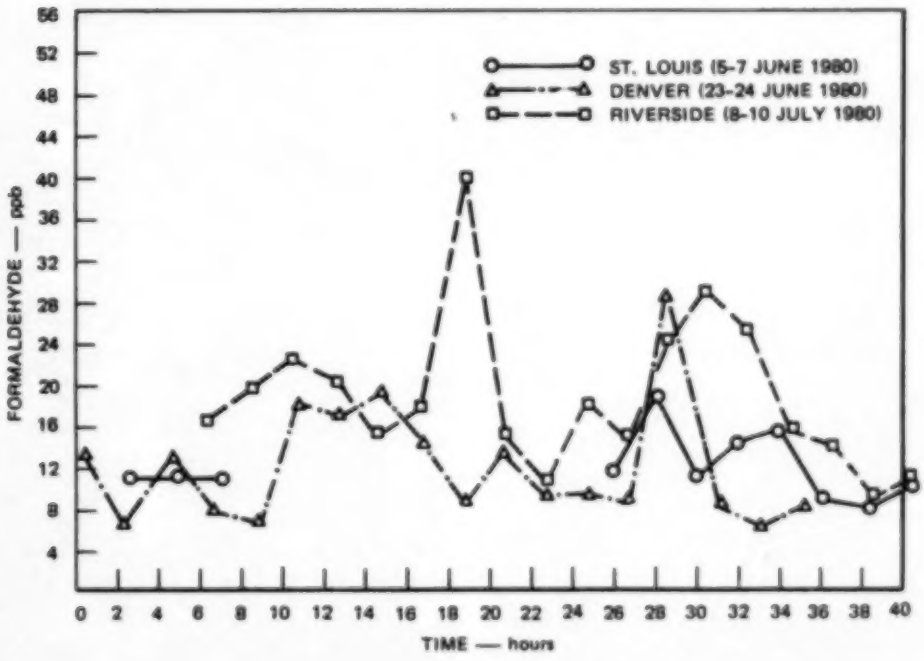


Figure 26. Atmospheric concentrations of formaldehyde.

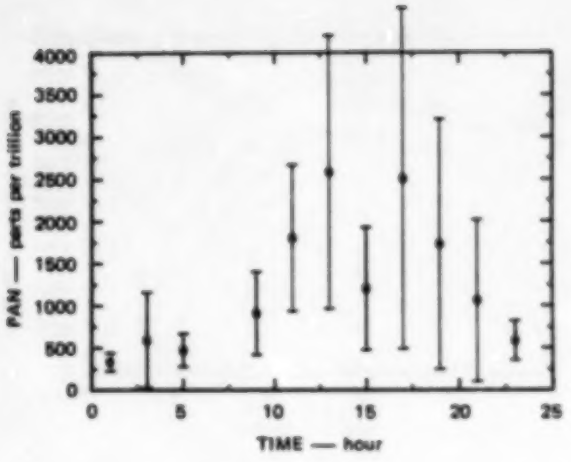


Figure 27. Mean diurnal variation of peroxyacetyl nitrate (PAN) at Riverside, CA, 2-12 July 1980.

SECTION 7

FUTURE RESEARCH PLANS

The second-year research effort was completed successfully as planned. To date data for a large number of selected toxic chemicals have been collected from seven cities:

- Los Angeles, California
- Phoenix, Arizona
- Oakland, California
- Houston, Texas
- St. Louis, Missouri
- Denver, Colorado
- Riverside, California.

In the third (final) year of this project, a significant emphasis will be placed on field measurements and on analysis and interpretation of the data set collected during this study. The major effort in the third year will be devoted to:

- Expanding the list of toxic chemicals to be measured
- Conducting additional field studies in selected U.S. cities
- Analyzing and interpreting all collected field data
- Preparing a final report.

During the end of the second year and early part of the third year of research efforts will be directed to developing measurement methods for ambient aldehydes and ketones (as well as formaldehyde, which was measured in the second year). A high-pressure liquid chromatograph (HPLC) has been acquired and will be utilized. The test methods are similar to those utilized by Kuwato et al. (1979). Attempts to identify currently unidentified species that have been found to be nearly ubiquitously present will continue, and we will try to improve the separation of chlorinated aromatics (especially $p\text{-}C_6H_4Cl_2$).

The following four cities have been tentatively identified as field site locations for the third year:

- New York City, New York
- Cleveland, Ohio
- Philadelphia, Pennsylvania
- Chicago, Illinois.

Three of these will be selected after discussions with the project officer. The literature search will continue as will the analysis of collected data. We expect to begin preparation of a comprehensive final report dealing with the abundance, intake, sources, sinks and effects of toxic chemicals.

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